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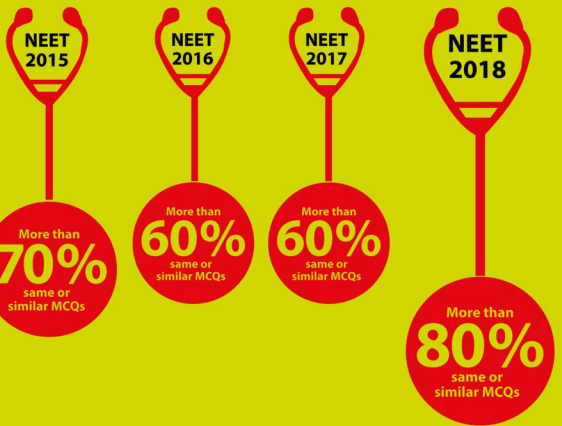

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CHEMISTRY today

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CONTENTS

TO OUR READERS

We are happy that intelligent students, teachers and other professionals continue to patronise Mathematics Today, Chemistry Today, Physics For You and Biology Today.

To them, we are addressing this open letter in view of increase in the cost of production and postage in the last seven years. All round spiralling prices have pushed production costs so high, that many in out fraternity find it impossible to continue business. We are compelled to raise the price to ₹ 40 from July 2018 issue.

We understand the pressure of cost on the student-teacher community in general but, we are hoping our readers will understand our problems and that we have no option but to comply with this unavoidable move.

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CHEMISTRY MUSING

PROBLEM SET 59

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.
The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET

1. When 1-pentyne (*A*) is treated with 4 N alcholic KOH at 175 °C, it is slowly converted into an equilibrium mixture of 1.3% of 1-pentyne (*A*), 95.2% 2-pentyne (*B*) and 3.5% of 1, 2-pentadiene (*C*). The equilibrium was maintained at 175 °C. Calculate ΔG° for the following equilibria:

$$B \rightleftharpoons A; \quad \Delta G^\circ_1 = ?$$
$$B \rightleftharpoons C; \quad \Delta G^\circ_2 = ?$$

ΔG°_1	ΔG°_2
(a) 16.178	16.178
(b) 15.869	12.266
(c) 17.125	12.123
(d) 12.282	17.185

2. Hyrdocarbon (*X*), C_7H_{12} on reaction with boron hydride followed by treatment with CH_3COOH yields (*A*). On reductive ozonolysis of (*A*) it yields a mixture of two aldehydes, (*B*) and (*C*). Of these, only (*B*) can undergo Cannizzaro reaction. (*A*) exists in two geometrical isomers, (*A* – 1) and (*A* – 2), of which (*A* – 2) is more stable. Give structure of (*X*).

(a) $CH_3-C\equiv C-CH_3$
(b) $(CH_3)_3C-C\equiv C-CH_3$
(c) $(CH_3)_3C-C\equiv C-C(CH_3)_3$
(d) $CH_3-CH_2-C\equiv C-CH_3$

3. A plant virus was found to consist of uniform cylindrical particles 100 Å in diameter and 4000 Å long. The virus has a specific volume 0.314 $cm^3\ g^{-1}$. If the virus particle is considered to be one molecule, what is its molecular weight?

(a) 10^{-6} g (b) 10^{-16} g
(c) 6.02×10^7 (d) 6.02×10^{17}

4. For M^{2+}/M and M^{3+}/M^{2+} system, the E° values for some metals are as follows :

Cr^{2+} / Cr	–0.9 V	Cr^{3+} / Cr^{2+}	–0.4 V
Mn^{2+} / Mn	–1.2 V	Mn^{3+} / Mn^{2+}	+1.5 V
Fe^{2+} / Fe	–0.4 V	Fe^{3+} / Fe^{2+}	+0.8 V

The order of ease to get oxidised will be

(a) Cr > Mn > Fe
(b) Mn > Fe > Cr
(c) Mn > Cr > Fe
(d) Fe > Cr > Mn

5. 0.093 g of $Na_2H_2EDTA.2H_2O$ is dissolved in 250 mL of aqueous solution. A sample of hard water containing Ca^{2+} and Mg^{2+} ions is titrated with the above EDTA solution using a buffer of NH_4OH + NH_4Cl using eriochrome black-T as indicator. 10 mL of the above EDTA solution requires 10 mL of hard water at equivalence point. Another sample of hard water is titrated with 10 mL of above EDTA solution using KOH solution (pH = 12). Using murexide indicator, it requires 40 mL of hard water at equivalence point. Calculate the amount of Mg^{2+} present in 1 L of hard water.

(a) 0.01 (b) 0.018
(c) 0.015 (d) 0.02

(Given: Mol. wt. (EDTA salt) = 372 g mol^{-1},
Mol. wt. ($CaCO_3$) = 100 g mol^{-1})

JEE ADVANCED

6. A 500 mL sample of an equilibrium mixture of gaseous N_2O_4 and NO_2 at 25 °C and 753 mmHg was allowed to react with enough water to make 250.0 mL of solution at 25 °C. Assume that all the dissolved N_2O_4 is converted to NO_2 which disproportionates in water yielding a solution of nitrous acid and nitric acid. Assume further that disproportionation reaction goes to completion and that none of the nirtous acid disproportionates. The equilibrium constant (K_p) for, $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ is 0.113 at 25°C. What is pH of the solution?

COMPREHENSION

i. Compound (X) $(C_{18}H_{20}O)$ $\xrightarrow{O_3/\text{Red.}}$ $(A)\,(C_{10}H_{12}O) + (B)\,(C_8H_8O_2)$

ii. Compound (A) (Shows +ve iodoform test) $\xrightarrow{NH_2OH}$ Oxime (C) $(C_{10}H_{13}ON)$ $\xrightarrow[(ii)\ H_3O^+]{(i)\ PCl_5/\text{ether}}$ $CH_3-COOH + (C_8H_{11}N)$ (D)

Phthalic acid $\xleftarrow{[O]}$ Aromatic alcohol (E) $(C_8H_{10}O)$ $\xleftarrow[\text{at } 0\,^\circ C]{HNO_2}$ (D)

iii. Compound (B) $\xrightarrow[\text{Oxid.}]{\text{Mild}}$ $(C_8H_8O_3)$ Acid (F) $\xrightarrow{HI}$ HO–C$_6$H$_4$–COOH + CH_3I

iv. Compound (X) has the highest melting point among its isomers.

7. Compound (B) is

(a) MeO–C$_6$H$_4$–COOH

(b) MeO–C$_6$H$_4$–CHO

(c) MeO–C$_6$H$_4$–CH_2OH

(d) HO–C$_6$H$_4$–CHO

8. Compound (E) is:

(a) 

(b) HOH_2C–C$_6$H$_4$–CH_2OH

(c) 

(d) $HOCH_2$–C$_6$H$_4$–Me

INTEGER VALUE

9. Iron (II) oxide, FeO, crystal has a cubic structure and each edge of the unit cell is 5.0 Å. Taking density of the oxides as 4.0 g cm^{-3}, calculate the number of Fe^{2+} ions present in each unit cell.

10. The complex compound $K_4[Fe(CN)_6]$ is 45% dissociated in 0.1 M aqueous solution of the complex at 27 °C. What would be the osmotic pressure of the solution approximately?

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1. The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy list :

(1) $n = 4, l = 2, m_l = -2, m_s = -1/2$
(2) $n = 3, l = 2, m_l = 1, m_s = +1/2$
(3) $n = 4, l = 1, m_l = 0, m_s = +1/2$
(4) $n = 3, l = 2, m_l = -2, m_s = -1/2$
(5) $n = 3, l = 1, m_l = -1, m_s = +1/2$
(6) $n = 4, l = 1, m_l = 0, m_s = +1/2$

(a) 1 > 2 > 3 > 4 = 5 > 6
(b) 1 > 2 > 3 = 6 > 4 = 5
(c) 1 > 3 = 6 > 4 = 2 > 5
(d) 1 > 3 = 6 > 4 = 5 > 2

2. Which of the following is commercially known as oxone?

(a) $Na_2O_2 + HCl$ (b) $Na_2O + HCl$
(c) $Na_2O_2 + Na_2O$ (d) None of these

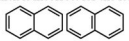
3. Assume that the decomposition of HNO_3 can be represented by the following equation :

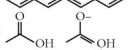
$4HNO_{3(g)} \rightleftharpoons 4NO_{2(g)} + 2H_2O_{(g)} + O_{2(g)}$

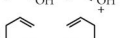
and the reaction approaches equilibrium at 400 K temperature and 30 atm pressure. At equilibrium partial pressure of HNO_3 is 2 atm. Calculate K_c in $(mol/L)^3$ at 400 K.

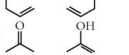
(a) 4 (b) 8 (c) 16 (d) 32

4. Which is incorrect for the following pairs?

(a)  Resonance

(b)  Equilibrium

(c)  Equilibrium

(d)  Tautomerism

5. Consider the following reaction,

$H_3C - \underset{D}{CH} - \underset{CH_3}{CH} - CH_3 + \dot{B}r \longrightarrow$ 'X' + HBr

Identify the structure of the major product 'X'.

(a) $CH_3 - \underset{D}{CH} - \underset{CH_3}{\dot{C}H_2}$

(b) $CH_3 - \underset{D}{CH} - \underset{CH_3}{\dot{C}} - CH_3$

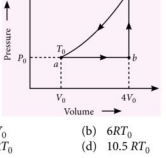
(c) $CH_3 - \underset{D}{\dot{C}} - \underset{CH_3}{CH} - CH_3$

(d) $CH_3 - \underset{\dot{C}H_3}{CH} - CH_3$

6. A silver coin weighing 11.34 g was dissolved in nitric acid. When sodium chloride was added to the solution all the silver (present as $AgNO_3$) was precipitated as silver chloride. The weight of the precipitated silver chloride was 14.35 g. Calculate the percentage of silver in the coin.

(a) 4.8 % (b) 95.2 %
(c) 90 % (d) 80 %

7. One mole of an ideal monoatomic gas is go through the cycle shown in figure. Then, the change in the internal energy in expanding the gas from *a* to *c* along the path *abc* is



(a) $3P_0V_0$ (b) $6RT_0$
(c) $4.5\,RT_0$ (d) $10.5\,RT_0$

8. Calculate de-Broglie wavelength of an electron travelling with 1% of the speed of light.

(a) 2.73×10^{-24} m (b) 2.43×10^{-10} m
(c) 242.2×10^{-10} m (d) None of these

9. A gas X_2Y_4 at 35 °C has *rms* speed 12 m s^{-1}. On heating the gas twice to the original absolute temperature, the dimer totally dissociated to give monomer. What is the *rms* speed of XY_2 molecule at the given elevated temperature?

(a) 24 m s^{-1} (b) 30 m s^{-1}
(c) 18 m s^{-1} (d) 32 m s^{-1}

10. If the molecule of HCl is totally polar, the expected value of dipole moment is 6.12 D but the experimental value of dipole moment is 1.03 D. Calculate the percentage ionic character.

(a) 17 (b) 83
(c) 50 (d) 0

11. In silicon dioxide,

(a) there are double bonds between silicon and oxygen atoms
(b) silicon atom is bonded to two oxygen atoms
(c) each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
(d) each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms.

12. In the estimation of carbon and hydrogen by combustion method which of the following is/are correct?

(I) A spiral of copper is introduced at the right extreme of combustion tube if the organic compound contains nitrogen.
(II) A spiral of silver is introduced if the organic compound contains halogens.
(III) The copper oxide in the combustion tube is replaced by lead chromate if the organic compound contains sulphur.

(a) (I) and (II) are correct.
(b) (I) and (III) are correct.
(c) (II) and (III) are correct.
(d) All are correct.

13. Standard electrode potentials of redox couples, A^{2+}/A, B^{2+}/B, C^{2+}/C and D^{2+}/D are 0.3 V, – 0.5 V, –0.75 V and 0.9 V respectively. Which of these is best oxidising agent and reducing agent respectively?

(a) D^{2+}/D and B^{2+}/B (b) B^{2+}/B and D^{2+}/D
(c) D^{2+}/D and C^{2+}/C (d) C^{2+}/C and D^{2+}/D

14. 0.765 g of an acid gives 0.535 g of CO_2 and 0.138 g of H_2O. Then the ratio of the percentage of carbon and hydrogen is

(a) 19 : 2 (b) 18 : 11
(c) 20 : 17 (d) 1 : 7

15. How many kilograms of wet NaOH, containing 12% water, are required to prepare 60 litres of 0.50 N solution?

(a) 1.36 kg (b) 1.50 kg
(c) 2.40 g (d) 3.16 kg

SOLUTIONS

1. **(c)** : (1) $4d(n + l = 4 + 2 = 6)$
(2) $3d(n + l = 3 + 2 = 5)$
(3) $4p(n + l = 4 + 1 = 5)$
(4) $3d(n + l = 3 + 2 = 5)$
(5) $3p(n + l = 3 + 1 = 4)$
(6) $4p(n + l = 4 + 1 = 5)$
Higher the value of $n + l$, higher will be the energy of orbital. If two orbitals have same $n + l$ value then the orbital having higher n value will possess higher energy. Therefore, the required order is (5) < (2) = (4) < (6) = (3) < (1).

2. **(a)**

3. **(d) :** $P_{Total} = P_{HNO_3} + P_{NO_2} + P_{H_2O} + P_{O_2}$

$\because \quad P_{NO_2} = 4P_{O_2}$ and $P_{H_2O} = 2P_{O_2}$

$\therefore \quad P_{Total} = P_{HNO_3} + 7P_{O_2}$

$\Rightarrow \quad 30 - 2 = P_{O_2} \times 7$

$$\Rightarrow \quad P_{O_2} = \frac{28}{7} = 4$$

$$K_P = \frac{P^4_{NO_2} \cdot P^2_{H_2O} \cdot P_{O_2}}{P^4_{HNO_3}}$$

$$= \frac{(4\times4)^4 \times (2\times4)^2 \times 4}{2^4} = 2^{20}$$

$$K_P = K_c(RT)^{\Delta n_g} = K_c(0.08 \times 400)^3$$

$$\Rightarrow \quad K_c = \frac{2^{20}}{(32)^3} = 32$$

4. **(b) :** The pair has resonance.

5. **(b) :** Br is less reactive but more selective, therefore the most stable 3° free radical will be the major product.

6. **(b) :** $\underset{108\text{ g}}{Ag} + 2HNO_3 \longrightarrow AgNO_3 + NO_2 + H_2O$

$$\underset{108\text{ g}}{AgNO_3} + NaCl \longrightarrow \underset{143.5\text{ g}}{AgCl} + NaNO_3$$

$\therefore$ 143.5 g of silver chloride would be precipitated by 108 g of silver.

or 14.35 g of silver chloride would be precipitated by 10.8 g of silver.

$\because$ 11.34 g of silver coin contains 10.8 g of pure silver.

$\therefore$ 100 g of silver coin contains

$$\frac{10.8}{11.34} \times 100 = 95.2\%$$

7. **(d) :** $PV = nRT$

At point c,

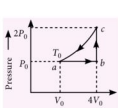
$2P_0 \times 4V_0 = 1 \times RT_c$

$$T_c = \left[\frac{8P_0V_0}{R}\right]$$

At point a,

$P_0V_0 = 1 \times RT_0$

$$T_0 = \frac{P_0V_0}{R} \text{ or } T_c = 8T_0$$



Change in internal energy = $[nC_V dT]$

For path a to $b = 1 \times \frac{3}{2}R \times [3T_0] = \frac{9}{2}RT_0$

For path b to $c = 1 \times \frac{3}{2}R \times [4T_0] = 6RT_0$

Total change $= \frac{9}{2}RT_0 + 6RT_0 = \frac{21RT_0}{2} = 10.5RT_0$

So, total change in internal energy, $\Delta U = 10.5\ RT_0$

8. **(b) :** One per cent of the speed of light is (v)

$$= \left(\frac{1}{100}\right)(3\times10^8 \text{ m s}^{-1}) = 3\times10^6 \text{ m s}^{-1}$$

Momentum of the electron $(p) = mv$

$= (9.11 \times 10^{-31}\text{ kg})(3 \times 10^6\text{ m s}^{-1})$

$= 2.73 \times 10^{-24}\text{ kg m s}^{-1}$

The de-Broglie wavelength of this electron is

$$\lambda = \frac{h}{p} = \frac{6.626\times10^{-34}\text{ kg m}^2\text{ s}^{-1}}{2.73\times10^{-24}\text{ kg m s}^{-1}}$$

$\lambda = 2.43 \times 10^{-10}$ m

9. **(a) :** *rms* velocity $(c) = \sqrt{\frac{3RT}{M}}$

Given temperature, $T_1 = 308$ K

Elevated temperature, $T_2 = 616$ K

rms velocity at temperature 308 K $(c_1) = \sqrt{\frac{3RT_1}{M_1}}$

rms velocity at temperature 616 K $(c_2) = \sqrt{\frac{3RT_2}{M_2}}$

The ratio of *rms* velocities,

$$\frac{c_2}{c_1} = \sqrt{\frac{T_2}{T_1}\frac{M_1}{M_2}}$$

$$\underset{\text{Mass} = M_1}{X_2Y_4} \rightleftharpoons \underset{\text{Mass} = M_2}{2XY_2}$$

or $M_1 = 2M_2$

$$\therefore \quad \frac{c_2}{c_1} = \sqrt{\frac{616}{308}\times\frac{2M_2}{M_2}} = 2$$

$c_2 = 2 \times c_1 = 2 \times 12\text{ m s}^{-1} = 24\text{ m s}^{-1}$

10. **(a) :** Percentage ionic character

$$= \frac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}} \times 100$$

$$= \frac{1.03}{6.12} \times 100 = 16.83 = 17\%$$

11. **(d) :** In SiO_2 (quartz), each O-atom is shared between two silicon atom and each Si atom is surround by four-oxygen atoms.

12. (d) : When organic compound contains nitrogen, upon combustion it will produce oxides of nitrogen soluble in KOH solution. The copper will convert them into N_2.

$2NO + 2Cu \longrightarrow 2CuO + N_2$

$2NO_2 + 4Cu \longrightarrow 4CuO + N_2$, etc.

Halogens will be removed as AgX. In case of sulphur, SO_2 formed will be removed as $PbSO_4$.

13. (c) : The redox couple with maximum reduction potential will be best oxidising agent and with minimum reduction potential will be the best reducing agent.

14. (a) : Mass of the organic compound (w) = 0.765 g

Mass of the carbon dioxide formed (x) = 0.535 g

Mass of the water formed (y) = 0.138 g

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{y}{w} \times 100$$

$$= \frac{2}{18} \times \frac{0.138}{0.765} \times 100 = 2\%$$

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{x}{w} \times 100$$

$$= \frac{12}{44} \times \frac{0.535}{0.765} \times 100 = 19\%$$

So, the ratio of C : H = 19 : 2

15. (a) : One litre of 0.50 N NaOH contains

$= 0.50 \times 40$ g$= 20$ g $= 0.020$ kg

$\therefore$ 60 litres of 0.50 N NaOH contain

$= 0.020 \times 60$ kg $= 1.20$ kg NaOH

Since, the given NaOH contains 12% water, the amount of pure NaOH in 100 kg of the given NaOH = 100 – 12 = 88 kg

Thus, 88 kg of pure NaOH is present in 100 kg wet NaOH.

$\therefore$ 1.20 kg of pure NaOH is present in

$$= \frac{100}{88} \times 1.20 = 1.36 \text{ kg wet NaOH}$$

Scientist of the Month

Georg Wittig

(16 June, 1897 - 26 August, 1987)

Early life and Education

Wittig was born in Berlin, Germany and shortly after his birth moved with his family to Kassel, where his father was professor at the applied arts high school.

After being an English prisoner of war from 1918 till 1919, Wittig found it hard to restart his chemistry studies owing to overcrowding at the universities. By a direct plea to Karl von Auwers, who was professor for organic chemistry at the University of Marburg at the time, he was able to resume university study and after 3 years was awarded the Ph.D. in organic chemistry. He started his academic career as lecturer and become professor to the TU Braunschweig in 1932.

In 1937, Hermann Staudinger offered Wittig a position at the University of Freiburg, partly because he knew Wittig from his book on stereochemistry in which he supported Staudinger's highly criticized theory of macromolecules. The foundations of carbanion chemistry were laid during Wittig's time in Freiburg.

In 1944, he succeeded the head of the organic chemistry department Wilhelm Schlenk at the University of Tübingen.

He worked at the University of Heidelberg even after his retirement in 1967 and published papers until 1980.

Contribution

He reported a method for synthesis of alkenes from aldehydes and ketones using compounds called phosphonium ylides in the Wittig reaction.

Wittig's contributions also include the preparation of phenyllithium and the discovery of the 1,2-Wittig rearrangement and the 2,3-Wittig rearrangement.

Wittig was well known in the chemistry community for being a consummate experimenter and observer of chemical transformations, while caring very little for the theoretical and mechanistic underpinnings of the work he produced.

Awards & Honours

- He shared the Nobel prize in chemistry with Herbert C. Brown in 1979.

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1. Lowering of vapour pressure in 1 molal aqueous solution at 100 °C is

(a) 13.44 mm Hg (b) 14.12 mm Hg
(c) 31.2 mm Hg (d) 35.2 mm Hg

2. $FeCr_2O_4 + Na_2CO_3 + O_2 \xrightarrow{\text{Fusion}} [X] \xrightarrow[H_2O]{H^+} [Y] \xrightarrow[H_2O_2]{H^+} [Z]$

Which of the following statements is true for the compounds [X], [Y] and [Z]?

(a) In all three compounds, the chromium is in +6 oxidation state.
(b) [Z] is a deep blue-violet coloured compound which decomposes rapidly in aqueous solution into Cr^{3+} and dioxygen.
(c) Saturated solution of [Y] gives bright orange red compound, chromic anhydride with concentrated H_2SO_4.
(d) All of these.

3. The major organic product formed from the following reaction is

(a)
(b)
(c)
(d) 

4. **Statement 1 :** is named as tetrakis(ethylene diammine)-μ-hydroxo-μ-imido dicobalt (III) ion.

Statement 2 : In naming polynuclear complexes *i.e.*, containing two or more metal atoms joined by bridging ligands, the word μ is added with hyphen before the name of such ligands.

(a) If both Statement 1 and Statement 2 are True and the Statement 2 is a correct explanation of the Statement 1.
(b) If both Statement 1 and Statement 2 are True but Statement 2 is not a correct explanation of the Statement 1.
(c) If Statement 1 is True but the Statement 2 is False.
(d) If both Statement 1 and Statement 2 are False.

5. In the following sequence of reactions,

$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[\text{Ether}]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$

The compound *D* is

(a) propanal (b) butanal
(c) *n*-butyl alcohol (d) *n*-propyl alcohol.

6. Consider the following perhalate ions in acidic medium, ClO_4^- (I), BrO_4^- (II), IO_4^- (III).
Arrange these in the decreasing order of oxidising power.
(a) I > II > III (b) I > III > II
(c) II > I > III (d) II > III > I

7. **Statement 1 :** The following compounds given below are soluble in NaOH.

$CH_3CH_2NO_2$, $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NO_2$ and

$CH_3-\underset{\displaystyle NO_2}{\underset{|}{CH}}-CH_2-CH_3$

Statement 2 : All above compounds have lower boiling point than CH_3NO_2.
(a) If both Statement 1 and Statement 2 are true and the Statement 2 is a correct explanation of the Statement 1.
(b) If both Statement 1 and Statement 2 are true but Statement 2 is not a correct explanation of the Statement 1.
(c) If Statement 1 is true but the Statement 2 is false.
(d) If both Statement 1 and Statement 2 are false.

8. In a solid, oxide ions are arranged in *ccp*. Cations *A* occupy one-sixth of the tetrahedral voids and cations *B* occupy one-third of the octahedral voids. The formula of the compound is
(a) ABO_3 (b) AB_2O_3
(c) A_2BO_3 (d) $A_2B_2O_3$

9. In the given reaction :
$CH_3-CH_2-COOH \xrightarrow[\text{(ii) } Br_2/\Delta]{\text{(i) } AgNO_3} [X]$. $[X]$ will be
(a) ethyl bromide (b) propyl bromide
(c) propyl propanoate (d) all of these.

10. The time taken for the completion of $3/4^{th}$ of a first order reaction is
(a) $\left(\frac{2.303}{k}\right)\log 3/4$ (b) $\left(\frac{2.303}{k}\right)\log 4$
(c) $\left(\frac{2.303}{k}\right)\log 1/4$ (d) $\left(\frac{2.303}{0.75}\right)\log k$

11. The volume of a colloidal particle, V_C as compared to the volume of a solute particle in a true solution V_S, could be
(a) $\frac{V_C}{V_S} \simeq 10^3$ (b) $\frac{V_C}{V_S} \simeq 10^{-3}$
(c) $\frac{V_C}{V_S} = 10^{23}$ (d) $\frac{V_C}{V_S} \simeq 1$

12. Among the following compounds which can be dehydrated very easily?
(a) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$
(b) $CH_3CH_2CH_2CHCH_3$ (OH)
(c) $CH_3CH_2CH_2CH_2CH_2OH$
(d) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2OH$

13. The ionic radius of Cr is minimum in which of the following compounds?
(a) CrF_3 (b) $CrCl_3$
(c) Cr_2O_3 (d) K_2CrO_4

14. Which of the following is not a function of proteins?
(a) Nail formation
(b) Skin formation
(c) Muscle formation
(d) Providing energy for metabolism

15. When $CuSO_4$ is electrolysed using platinum electrodes
(a) copper is liberated at cathode, sulphur at anode
(b) copper is liberated at cathode, oxygen at anode
(c) sulphur is liberated at cathode, oxygen at anode
(d) oxygen is liberated at cathode, copper at anode.

SOLUTIONS

1. **(a) :** Molality and mole fraction are related as follows :

$$m = \frac{x_B \times 1000}{(1-x_B)m_A}$$

$$1 = \frac{x_B \times 1000}{(1-x_B)\times 18}$$

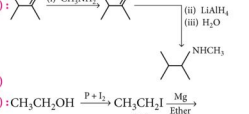
x_B = mole fraction of solute
m_A = molar mass of solvent
$x_B = 0.0176$, $x_A = 0.9824$
$p = p_0 x_A$
$p = 760 \times 0.9824 = 746.624$
$\Delta p = p_0 - p = 760 - 746.624 \simeq 13.4$ mm Hg

2. **(d)** : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Fusion}} 8\underset{\text{'X'}}{Na_2\overset{+6}{C}rO_4}$

$$\underset{\text{'X'}}{Na_2\overset{+6}{C}rO_4} \xrightarrow[H_2O]{H^+} \underset{\text{'Y'}}{Na_2\overset{+6}{C}r_2O_7} \xrightarrow{H^+/H_2O_2} \underset{\substack{\text{'Z'}\\ \text{(Deep blue violet)}}}{2\overset{+6}{C}rO(O_2)_2} \xrightarrow{H_2O} Cr^{3+} + H_2O + O_2$$

$$Na_2Cr_2O_7 + H_2SO_4 \longrightarrow \underset{\substack{\text{(Chromic}\\ \text{anhydride)}}}{2CrO_3} + Na_2SO_4 + H_2O$$

3. **(b)** :



4. **(b)**

5. **(d)** : $CH_3CH_2OH \xrightarrow{P+I_2} \underset{(A)}{CH_3CH_2I} \xrightarrow{\text{Mg / Ether}}$

$$\underset{(B)}{CH_3CH_2MgI} \xrightarrow{HCHO} H-\overset{\displaystyle CH_2CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OMgI \xrightarrow{H_2O}$$

$$H-\overset{\displaystyle CH_2CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OH$$

(*D*) *n*-propyl alcohol

6. **(d)** : Standard reduction potential (in volts) of the perhalate ions are given below :

$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O$; $E^\circ = 1.19$ V

$BrO_4^- + 2H^+ + 2e^- \longrightarrow BrO_3^- + H_2O$; $E^\circ = 1.74$ V

$IO_4^- + 2H^+ + 2e^- \longrightarrow IO_3^- + H_2O$; $E^\circ = 1.65$ V

More the standard reduction potential, the more is tendency of perhalite ion to undergo reduction and more stronger it will be as an oxidising agent.

7. **(c)**

8. **(a)** : Suppose number of O^{2-} ions in $ccp = n$

$\therefore$ Number of octahedral voids $= n$

and number of tetrahedral voids $= 2n$

Cation A present $= \frac{2n}{6} = \frac{n}{3}$

Cation B present $= \frac{n}{3}$

$\therefore \quad A : B : O^{2-} = \frac{n}{3} : \frac{n}{3} : n = \frac{1}{3} : \frac{1}{3} : 1 = 1 : 1 : 3$

Hence, formula $= ABO_3$

9. **(a)** : $CH_3CH_2COOH \xrightarrow[(ii)\ Br_2/\Delta]{(i)\ AgNO_3} CH_3CH_2Br$

10. **(b)** : $t = \frac{2.303}{k}\log\frac{a}{a-x}$

Let initial concentration be 1,

then $t = \frac{2.303}{k}\log\frac{1}{1-3/4} \Rightarrow \frac{2.303}{k}\log 4$

11. **(a)** : Size of colloidal particles = 1 mμ to 100 mμ

$V_C = \frac{4}{3}\pi r^3 \Rightarrow V_C = \frac{4}{3}\pi(10)^3$

Size of true solution particles = 1 mμ

$V_S = \frac{4}{3}\pi(1)^3$

Hence, $\frac{V_C}{V_S} = 10^3$

12. **(a)** : 3-Methylpentan-3-ol will be dehydrated most readily since it produces tertiary carbonium ion as intermediate.

$$CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2-CH_3 \xrightarrow{H^+} CH_3-CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{+}{C}}}-CH_2-CH_3$$

3° Carbocation

13. **(d)** : Cr has maximum oxidation number (+6) in K_2CrO_4 and thus, has minimum ionic radius.

14. **(d)** : Proteins do not provide energy for metabolism.

15. **(b)** : $CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$

$H_2O \rightleftharpoons H^+ + OH^-$

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

At anode : $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

NEET

SOLVED PAPER 2018

Hurray!! We are happy to inform our readers that out of the 45 questions asked in NEET 2018, approximately 80% questions were either exactly same or of similar type from the **MTG Books**. Hurray!!

Here, the references of few are given :

S. No.	MTG Books	Q. No.	Pg. No.
2	NEET Champion	96	338
11	NCERT Fingertips	7	164
12	NEET Guide	15	28
18	NEET Champion	28	235
24	NEET Guide	166	192
25	NEET Champion	243	162
26	NEET Champion	88	106
27	NEET Guide	8	257
29	NEET Guide	5	257

S. No.	MTG Books	Q. No.	Pg. No.
31	NEET Champion	22	190
32	NEET Champion	97	155
33	NEET Champion	86	105
34	NEET Guide	121	102
35	NEET Guide	108	152
40	NEET Champion	166	206
42	NEET Champion	81	175
45	NCERT Fingertips	3	245

and more such questions .....

1. A mixture of 2.3 g formic acid and 4.5 g oxalic acid is treated with conc. H_2SO_4. The evolved gaseous mixture is passed through KOH pellets. Weight (in g) of the remaining product at STP will be
(a) 1.4 (b) 3.0 (c) 2.8 (d) 4.4

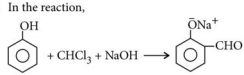
2. Nitration of aniline in strong acidic medium also gives *m*-nitroaniline because
(a) inspite of substituents nitro group always goes to only *m*-position
(b) in electrophilic substitution reactions amino group is *meta* directive
(c) in absence of substituents nitro group always goes to *m*-position
(d) in acidic (strong) medium aniline is present as anilinium ion.

3. Which of the following oxides is most acidic in nature?
(a) MgO (b) BeO (c) BaO (d) CaO

4. The difference between amylose and amylopectin is
(a) amylopectin have 1 → 4 α-linkage and 1 → 6 α-linkage
(b) amylose have 1 → 4 α-linkage and 1 → 6 β-linkage
(c) amylopectin have 1 → 4 α-linkage and 1 → 6 β-linkage
(d) amylose is made up of glucose and galactose.

5. Regarding cross-linked or network polymers, which of the following statements is incorrect?
(a) They contain covalent bonds between various linear polymer chains.
(b) They are formed from bi- and tri-functional monomers.
(c) Examples are bakelite and melamine.
(d) They contain strong covalent bonds in their polymer chains.

6. In the reaction,



the electrophile involved is
(a) dichloromethyl cation ($\overset{+}{C}HCl_2$)
(b) formyl cation ($\overset{+}{C}HO$)
(c) dichloromethyl anion ($\overset{-}{C}HCl_2$)
(d) dichlorocarbene ($:\!CCl_2$)

7. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their
   (a) formation of intramolecular H-bonding
   (b) formation of carboxylate ion
   (c) more extensive association of carboxylic acid via van der Waals' forces of attraction
   (d) formation of intermolecular H-bonding.

8. Compound A, $C_8H_{10}O$, is found to react with NaOI (produced by reacting Y with NaOH) and yields a yellow precipitate with characteristic smell. A and Y are respectively
   (a) H_3C–C$_6$H$_4$–CH_2–OH and I_2
   (b) C$_6$H$_5$–CH_2–CH_2–OH and I_2
   (c) C$_6$H$_5$–CH(OH)–CH_3 and I_2
   (d) CH_3–C$_6$H$_4$–OH and I_2

9. The correct difference between first and second order reactions is that
   (a) the rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations
   (b) the half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$
   (c) a first-order reaction can be catalysed; a second-order reaction cannot be catalysed
   (d) the rate of a first-order reaction does depend on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations.

10. Among CaH_2, BeH_2, BaH_2, the order of ionic character is
    (a) $BeH_2 < CaH_2 < BaH_2$
    (b) $CaH_2 < BeH_2 < BaH_2$
    (c) $BeH_2 < BaH_2 < CaH_2$
    (d) $BaH_2 < BeH_2 < CaH_2$

11. Consider the change in oxidation state of bromine corresponding to different emf values as shown in the given diagram :

$$BrO_4^- \xrightarrow{1.82\ V} BrO_3^- \xrightarrow{1.5\ V} HBrO$$
$$Br^- \xleftarrow{1.0652\ V} Br_2 \xleftarrow{1.595\ V}$$

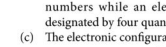
Then the species undergoing disproportionation is
(a) BrO_3^- (b) BrO_4^- (c) Br_2 (d) HBrO

12. In which case is number of molecules of water maximum?
    (a) 18 mL of water (b) 0.18 g of water
    (c) 0.00224 L of water vapours at 1 atm and 273 K
    (d) 10^{-3} mol of water

13. Magnesium reacts with an element (X) to form an ionic compound. If the ground state electronic configuration of (X) is $1s^2\ 2s^2\ 2p^3$, the simplest formula for this compound is
    (a) Mg_2X_3 (b) MgX_2 (c) Mg_2X (d) Mg_3X_2

14. Iron exhibits *bcc* structure at room temperature. Above 900 °C, it transforms to *fcc* structure. The ratio of density of iron at room temperature to that at 900 °C (assuming molar mass and atomic radii of iron remains constant with temperature) is
    (a) $\frac{\sqrt{3}}{\sqrt{2}}$ (b) $\frac{4\sqrt{3}}{3\sqrt{2}}$ (c) $\frac{3\sqrt{3}}{4\sqrt{2}}$ (d) $\frac{1}{2}$

15. Which one is a wrong statement?
    (a) Total orbital angular momentum of electron in *s*-orbital is equal to zero.
    (b) An orbital is designated by three quantum numbers while an electron in an atom is designated by four quantum numbers.
    (c) The electronic configuration of N atom is



    (d) The value of m for d_z^2 is zero.

16. Consider the following species : CN^+, CN^-, NO and CN. Which one of these will have the highest bond order?
    (a) NO (b) CN^- (c) CN^+ (d) CN

17. Which of the following statements is not true for halogens?
    (a) All form monobasic oxyacids.
    (b) All are oxidizing agents.
    (c) All but fluorine show positive oxidation states.
    (d) Chlorine has the highest electron-gain enthalpy.

18. Which one of the following elements is unable to form MF_6^{3-} ion?
    (a) Ga (b) Al (c) B (d) In

19. In the structure of ClF_3, the number of lone pairs of electrons on central atom 'Cl' is
(a) one (b) two (c) four (d) three.

20. Considering Ellingham diagram, which of the following metals can be used to reduce alumina?
(a) Fe (b) Zn (c) Mg (d) Cu

21. The correct order of atomic radii in group 13 elements is
(a) B < Al < In < Ga < Tl
(b) B < Al < Ga < In < Tl
(c) B < Ga < Al < Tl < In
(d) B < Ga < Al < In < Tl

22. The correct order of N-compounds in its decreasing order of oxidation states is
(a) HNO_3, NO, N_2, NH_4Cl
(b) HNO_3, NO, NH_4Cl, N_2
(c) HNO_3, NH_4Cl, NO, N_2
(d) NH_4Cl, N_2, NO, HNO_3

23. On which of the following properties does the coagulating power of an ion depend?
(a) The magnitude of the charge on the ion alone
(b) Size of the ion alone
(c) Both magnitude and sign of the charge on the ion
(d) The sign of charge on the ion alone

24. Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations:

A. 60 mL $\frac{M}{10}$ HCl + 40 mL $\frac{M}{10}$ NaOH

B. 55 mL $\frac{M}{10}$ HCl + 45 mL $\frac{M}{10}$ NaOH

C. 75 mL $\frac{M}{5}$ HCl + 25 mL $\frac{M}{5}$ NaOH

D. 100 mL $\frac{M}{10}$ HCl + 100 mL $\frac{M}{10}$ NaOH

pH of which one of them will be equal to 1?
(a) *B* (b) *A* (c) *D* (d) *C*

25. The solubility of $BaSO_4$ in water is 2.42×10^{-3} g L^{-1} at 298 K. The value of its solubility product (K_{sp}) will be (Given molar mass of $BaSO_4$ = 233 g mol^{-1})
(a) 1.08×10^{-10} mol^2 L^{-2}
(b) 1.08×10^{-12} mol^2 L^{-2}
(c) 1.08×10^{-14} mol^2 L^{-2}
(d) 1.08×10^{-8} mol^2 L^{-2}

26. Given van der Waals' constant for NH_3, H_2, O_2 and CO_2 are respectively 4.17, 0.244, 1.36 and 3.59, which one of the following gases is most easily liquefied?
(a) NH_3 (b) H_2 (c) O_2 (d) CO_2

27. The compound *A* on treatment with Na gives *B*, and with PCl_5 gives *C*. *B* and *C* react together to give diethyl ether. *A*, *B* and *C* are in the order
(a) C_2H_5OH, C_2H_6, C_2H_5Cl
(b) C_2H_5OH, C_2H_5Cl, C_2H_5ONa
(c) C_2H_5Cl, C_2H_6, C_2H_5OH
(d) C_2H_5OH, C_2H_5ONa, C_2H_5Cl

28. Hydrocarbon (*A*) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms. (*A*) is
(a) $CH \equiv CH$ (b) $CH_2 = CH_2$
(c) $CH_3 - CH_3$ (d) CH_4

29. The compound C_7H_8 undergoes the following reactions :

$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$$

The product *C* is
(a) *m*-bromotoluene (b) *o*-bromotoluene
(c) 3-bromo-2,4,6-trichlorotoluene
(d) *p*-bromotoluene.

30. Which oxide of nitrogen is not a common pollutant introduced into the atmosphere both due to natural and human activity?
(a) N_2O_5 (b) NO_2 (c) N_2O (d) NO

31. For the redox reaction

$$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$$

The correct coefficients of the reactants for the balanced equation are

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	16	5	2
(b)	2	5	16
(c)	2	16	5
(d)	5	16	2

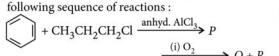
32. Which one of the following conditions will favour maximum formation of the product in the reaction $A_{2(g)} + B_{2(g)} \rightleftharpoons X_{2(g)}$, $\Delta_r H = -X$ kJ ?
(a) Low temperature and high pressure
(b) Low temperature and low pressure
(c) High temperature and high pressure
(d) High temperature and low pressure

33. The correction factor '*a*' to the ideal gas equation corresponds to
(a) density of the gas molecules
(b) volume of the gas molecules
(c) electric field present between the gas molecules
(d) forces of attraction between the gas molecules.

34. When initial concentration of the reactant is doubled, the half-life period of a zero order reaction
(a) is halved (b) is doubled
(c) is tripled (d) remains unchanged.

35. The bond dissociation energies of X_2, Y_2 and XY are in the ratio of 1 : 0.5 : 1. ΔH for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be
(a) 200 kJ mol^{-1} (b) 100 kJ mol^{-1}
(c) 800 kJ mol^{-1} (d) 400 kJ mol^{-1}

36. Identify the major products *P*, *Q* and *R* in the following sequence of reactions :



(a) P =  , Q =  ,
$R = CH_3CH_2$—OH

(b) P =  , Q =  ,
R = 

(c) P =  , Q =  ,
$R = CH_3CH(OH)CH_3$

(d) P =  , Q =  ,
$R = CH_3 - CO - CH_3$

37. Which of the following compounds can form a zwitter ion?
(a) Aniline (b) Acetanilide
(c) Benzoic acid (d) Glycine

38. The type of isomerism shown by the complex $[CoCl_2(en)_2]$ is
(a) geometrical isomerism
(b) coordination isomerism
(c) ionization isomerism
(d) linkage isomerism.

39. Which one of the following ions exhibits *d-d* transition and paramagnetism as well?
(a) CrO_4^{2-} (b) $Cr_2O_7^{2-}$
(c) MnO_4^- (d) MnO_4^{2-}

40. The geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ are
(a) square planar geometry and diamagnetic
(b) tetrahedral geometry and diamagnetic
(c) square planar geometry and paramagnetic
(d) tetrahedral geometry and paramagnetic.

41. Iron carbonyl, $Fe(CO)_5$ is
(a) tetranuclear (b) mononuclear
(c) trinuclear (d) dinuclear.

42. Match the metal ions given in Column I with the spin magnetic moments of the ions given in Column II and assign the correct code :

	Column-I		**Column-II**
A.	Co^{3+}	i.	$\sqrt{8}$ B.M.
B.	Cr^{3+}	ii.	$\sqrt{35}$ B.M.
C.	Fe^{3+}	iii.	$\sqrt{3}$ B.M.
D.	Ni^{2+}	iv.	$\sqrt{24}$ B.M.
		v.	$\sqrt{15}$ B.M.

	A	**B**	**C**	**D**
(a)	iv	v	ii	i
(b)	i	ii	iii	iv
(c)	iv	i	ii	iii
(d)	iii	v	i	ii

43. Which of the following is correct with respect to – *I* effect of the substituents? (*R* = alkyl)
(a) $-NH_2 < -OR < -F$
(b) $-NR_2 < -OR < -F$
(c) $-NH_2 > -OR > -F$
(d) $-NR_2 > -OR > -F$

44. Which of the following carbocations is expected to be most stable?

(a) 

(b) 

(c) 

(d) 

45. Which of the following molecules represents the order of hybridisation sp^2, sp^2, sp, sp from left to right atoms?

(a) $HC \equiv C - C \equiv CH$

(b) $CH_2 = CH - C \equiv CH$

(c) $CH_2 = CH - CH = CH_2$

(d) $CH_3 - CH = CH - CH_3$

SOLUTIONS

1. (c) : $HCOOH \xrightarrow[\text{conc. } H_2SO_4]{\text{Dehydrating agent}} CO + H_2O$

$n_i = \frac{2.3}{46} = \frac{1}{20}$		0	0
n_f	0		$\frac{1}{20}$	$\frac{1}{20}$

$H_2C_2O_4 \xrightarrow{\text{conc. } H_2SO_4} CO + CO_2 + H_2O$

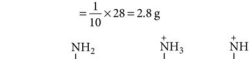
$n_i = \frac{4.5}{90} = \frac{1}{20}$		0	0	0
n_f	0		$\frac{1}{20}$	$\frac{1}{20}$	$\frac{1}{20}$

H_2O absorbed by H_2SO_4. Gaseous mixture (containing CO and CO_2) when passed through KOH pellets, CO_2 gets absorbed.

Moles of CO left (unabsorbed) $= \frac{1}{20} + \frac{1}{20} = \frac{1}{10}$

Mass of CO = moles × molar mass

$= \frac{1}{10} \times 28 = 2.8$ g

2. (d) : 

The reason for formation of an unexpected amount of *m*-nitroaniline is that under strongly acidic condition of nitration, most of the aniline is converted into anilinium ion and since, $-\overset{+}{N}H_3$ is a *m*-directing group, therefore, a large amount of *m*-nitroaniline is also obtained.

3. (b) : In metals, on moving down the group, metallic character increases, so basic nature increases hence most acidic will be BeO.

4. (a) : Amylose is a linear polymer of α-*D*-glucose held by C_1-C_4 glycosidic linkage whereas amylopectin is branched chain polymer of α-*D* glucose units in which chain is held by C_1-C_4 glycosidic linkage while branching occurs by C_1-C_6 glycosidic linkage.

5. (d) : Cross-linked or network polymers are usually formed from bi-functional and tri-functional monomers and contains strong covalent bonds between various linear polymer chains like melamine, bakelite, etc.

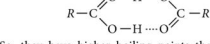
6. (d) : It is Reimer–Tiemann reaction. The electrophile formed is dichlorocarbene ($:CCl_2$) which is formed according to the following mechanism :

$CHCl_3 + \bar{O}H \rightleftharpoons \ddot{C}Cl_3 + H_2O$

$\ddot{C}Cl_3 \xrightarrow{-Cl^-\,(\alpha\text{-Elimination})} :CCl_2$

Dichlorocarbene (electrophile)

7. (d) : Due to the formation of intermolecular H-bonding, association occurs in carboxylic acids.

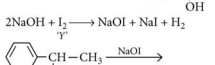


So, they have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass.

8. (c) : As the compound is giving yellow precipitate with NaOI that shows it is undergoing haloform reaction. Haloform reaction is shown by the compounds having $CH_3-\overset{\overset{O}{\|}}{C}-$ or $CH_3-\underset{\underset{OH}{|}}{CH}-$group.

Hence, the compound *A* is 

$2NaOH + I_2 \longrightarrow \underset{\text{'Y'}}{NaOI} + NaI + H_2$



9. (b) : For the first order reaction, $t_{1/2} = \frac{0.693}{k}$

which is independent of initial concentration $[A]_0$.

For second order reaction, $t_{1/2} = \frac{1}{k[A]_0}$

Half life depends on initial concentration of reactant.

10. (a) : $BeH_2 < CaH_2 < BaH_2$

On moving down the group, metallic character of metals increases. So, ionic character of metal hydrides increases. Hence, BeH_2 will be least ionic.

11. (d) : For a reaction to be spontaneous, E°_{cell} should be positive.

$HBrO \longrightarrow Br_2$ $\quad E^\circ = 1.595$ V, SRP (cathode)

$HBrO \longrightarrow BrO_3^-$ $\quad E^\circ = -1.5$ V, SOP (anode)

$2HBrO \longrightarrow Br_2 + BrO_3^-$

E°_{cell} = SRP (cathode) – SRP (anode)

$= 1.595 - 1.5$

$= 0.095$ V

$E^\circ_{cell} > 0 \Rightarrow \Delta G^\circ < 0$ (spontaneous)

12. (a) : (a)Mass of water = $V \times d = 18 \times 1 = 18$ g

Molecules of water = mole $\times N_A = \frac{18}{18} N_A = N_A$

(b) Molecules of water = mole $\times N_A = \frac{0.18}{18} N_A$

$= 10^{-2} N_A$

(c) Moles of water = $\frac{0.00224}{22.4} = 10^{-4}$

Molecules of water = mole $\times N_A = 10^{-4} N_A$

(d) Molecules of water = mole $\times N_A = 10^{-3} N_A$

13. (d) : Electronic configuration of X is $1s^2, 2s^2, 2p^3$. So, valency of X will be 3.

Magnesium ion = Mg^{2+}

Formula : Mg_3X_2

14. (c) : For *bcc* lattice : $Z = 2$, $a = \frac{4r}{\sqrt{3}}$

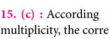
For *fcc* lattice : $Z = 4$, $a = 2\sqrt{2}\, r$

$$\therefore \frac{d_{R.T.}}{d_{900^\circ C}} = \frac{\left(\frac{ZM}{N_A a^3}\right)_{bcc}}{\left(\frac{ZM}{N_A a^3}\right)_{fcc}}$$

Given, molar mass and atom radii are constant.

$$= \frac{2}{4}\left(\frac{2\sqrt{2}r}{\frac{4r}{\sqrt{3}}}\right)^3 = \frac{3\sqrt{3}}{4\sqrt{2}}$$

15. (c) : According to Hund's rule of maximum multiplicity, the correct configuration of 'N' is



16. (b) : NO : $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^1 = (\pi^* 2p_y)^0$

$B.O. = \frac{10-5}{2} = 2.5$

CN^- : $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^2$

$B.O. = \frac{10-4}{2} = 3$

CN : $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^1$

$B.O. = \frac{9-4}{2} = 2.5$

CN^+ : $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2$

$B.O. = \frac{8-4}{2} = 2$

Hence, CN^- has highest bond order.

17. (c) : All halogen shows both positive and negative oxidation states while fluorine shows only positive oxidation state.

18. (c) : Boron does not have vacant *d*-orbitals in its valence shell, so it cannot extend its covalency beyond 4. *i.e.*, 'B' cannot form the ions like MF_6^{3-}.

19. (b) : The structure of ClF_3 is

Hence, Cl have 2 lone pairs of electrons.

20. (c) : Any metal oxide with lower value of ΔG° is more stable than a metal oxide with higher ΔG°. This implies that the metal oxide placed higher in the diagram can be reduced by the metal involved in the formation of the oxide placed lower in the diagram.

The relative tendency of the various metals to act as reducing agents is : Ca > Mg > Al > Cr > Zn > Fe > Cu. Thus, Mg being more reducing in nature, can reduce aluminium oxide (alumina).

21. (d)

22. (a) : $\overset{+5}{H}\overset{}{N}\overset{-2}{O_3}$, $\overset{+2}{N}\overset{-2}{O}$, $\overset{0}{N_2}$, $\overset{-3}{N}H_4Cl$

23 (c) : According to Hardy Schulze rule, the coagulating power of an electrolyte depends on both magnitude and sign of the charge of the effective ion or electrolyte.

24. (d) : pH = 1, so $[H^+] = 10^{-1}$

For acid base mixture: $N_1V_1 - N_2V_2 = N_3V_3$

(For NaOH and HCl, Normality = Molarity)

A. $M_1(H^+) = \dfrac{60\times\frac{1}{10} - 40\times\frac{1}{10}}{100} = 2\times10^{-3}$ M *i.e.* pH = 2.7

B. $M_2(H^+) = \dfrac{55\times\frac{1}{10} - 45\times\frac{1}{10}}{100} = \dfrac{1}{100} = 10^{-2}$ M *i.e.* pH = 2

C. $M_3(H^+) = \dfrac{75\times\frac{1}{5} - 25\times\frac{1}{5}}{100} = 10^{-1}$ M *i.e.* pH = 1

D. $M_4(H^+) = \dfrac{100\times\frac{1}{10} - 100\times\frac{1}{10}}{200} = 0$ *i.e.* pH = 7

25. (a) : Solubility of $BaSO_4$, $s = \dfrac{2.42\times10^{-3}}{233}$ mol L^{-1}

$= 1.04 \times 10^{-5}$ mol L^{-1}

$BaSO_4$ ionizes completely in the solution as :

$$\underset{s}{BaSO_{4(s)}} \rightleftharpoons \underset{s}{Ba^{2+}_{(aq)}} + \underset{s}{SO^{2-}_{4(aq)}}$$

$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}] = s^2$

$= (1.04 \times 10^{-5})^2 = 1.08 \times 10^{-10}$ mol^2 L^{-2}

26. (a) : van der Waals' constant '*a*' signifies the intermolecular forces of attraction between the particle of gas. So, higher the value of '*a*', easier will be the liquefaction of gas.

27. (d) :

$$C_2H_5OH \xrightarrow{Na} \underset{(B)}{C_2H_5O^-Na^+}$$
$$(A)$$

$$\downarrow PCl_5$$

$$C_2H_5Cl$$
$$(C)$$

$$C_2H_5O^-Na^+ + C_2H_5Cl \xrightarrow[\text{Williamson's synthesis}]{S_N2} C_2H_5OC_2H_5$$
$$(B) \qquad (C) \qquad \text{Diethyl ether}$$

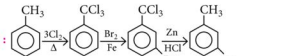
28. (d) :

$$CH_4 \xrightarrow{Br_2/h\nu} CH_3Br$$
$$(A)$$

$$\downarrow \text{Na/dry ether, Wurtz reaction}$$

$$CH_3-CH_3$$
(Less than 4 carbon atoms)

29. (a) :



(*A*) (*B*) (*C*) *m*-bromotoluene

30. (a)

31. (b) : The correct balanced equation is

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow$

$2Mn^{2+} + 10CO_2 + 8H_2O$

32. (a) : On increasing the pressure and decreasing the temperature, equilibrium will shift in forward direction.

33. (d)

34. (b) : $(t_{1/2})_{zero} = \dfrac{[A]_0}{2k}$

As the half-life of a zero order reaction is directly proportional to initial concentration.

$\therefore$ If $[A_0]$ = doubled then, $t_{1/2}$ = doubled.

35. (c) : Let B.E. of X_2, Y_2 and XY are x kJ mol^{-1}, 0.5x kJ mol^{-1} and x kJ mol^{-1} respectively.

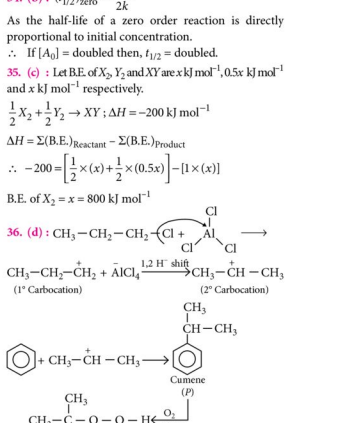
$\frac{1}{2}X_2 + \frac{1}{2}Y_2 \rightarrow XY\,;\ \Delta H = -200$ kJ mol^{-1}

$\Delta H = \Sigma(\text{B.E.})_{\text{Reactant}} - \Sigma(\text{B.E.})_{\text{Product}}$

$\therefore\ -200 = \left[\frac{1}{2}\times(x) + \frac{1}{2}\times(0.5x)\right] - [1\times(x)]$

B.E. of $X_2 = x = 800$ kJ mol^{-1}

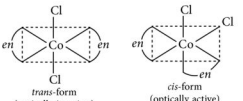
36. (d) :



(1° Carbocation) (2° Carbocation) (*P*) (*R*) (*Q*)

37. (d) : $HOOC-\underset{\text{Glycine}}{CH_2}-NH_2 \rightleftharpoons \underset{\text{Zwitter ion}}{^-OOC-CH_2-\overset{+}{N}H_3}$

38. (a) : $[CoCl_2(en)_2]$, exhibit geometrical isomerism, as the coordination number of Co is 6 and this compound has octahedral geometry.



39. (d) :

In CrO_4^{2-}	Cr^{+6}	$(n=0)$	diamagnetic
In $Cr_2O_7^{2-}$	Cr^{+6}	$(n=0)$	diamagnetic
In MnO_4^-	Mn^{+7}	$(n=0)$	diamagnetic
In MnO_4^{2-}	Mn^{+6}	$(n=1)$	paramagnetic

In MnO_4^{2-}, one unpaired electron(n) is present in *d*-orbital so, *d*-*d* transition is possible.

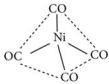
40. (b) : $Ni(28) : [Ar]3d^8 4s^2$

$\because$ CO is a strong field ligand, so, unpaired electrons get paired.

In $[Ni(CO)_4]$: $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}$ sp^3-hybridisation : $\boxed{\times\times}\ \boxed{\times\times}\boxed{\times\times}\boxed{\times\times}$

CO CO CO CO

Thus, the complex is sp^3 hybridised with tetrahedral geometry and diamagnetic in nature.



41. (b) : Based on the number of metal atoms present in a complex, they are classified as :

e.g. : $Fe(CO)_5$: mononuclear

$Co_2(CO)_8$: dinuclear

$Fe_3(CO)_{12}$: trinuclear

42. (a) : $Co^{3+} = [Ar]3d^6$, unpaired $e^-(n) = 4$

Spin magnetic moment $(\mu) = \sqrt{4(4+2)} = \sqrt{24}$ B.M.

$Cr^{3+} = [Ar]3d^3$, unpaired $e^-(n) = 3$

Spin magnetic moment $(\mu) = \sqrt{3(3+2)} = \sqrt{15}$ B.M.

$Fe^{3+} = [Ar]3d^5$, unpaired $e^-(n) = 5$

Spin magnetic moment $(\mu) = \sqrt{5(5+2)} = \sqrt{35}$ B.M.

$Ni^{2+} = [Ar]3d^8$, unpaired $e^-(n) = 2$

Spin magnetic moment $(\mu) = \sqrt{2(2+2)} = \sqrt{8}$ B.M.

43. (a, b) : $-I$ effect increases on increasing the electronegativity of atom.

$\therefore$ $-NH_2 < -OR < -F$ $\quad -I$ effect

Also, $-NR_2 < -OR < -F$ $\quad -I$ effect

44. (c) : $-NO_2$ group is *meta*-directing, thus will stabilize a electrophile at *m*-position.

45. (b) : $\overset{sp^2}{CH_2} = \overset{sp^2}{CH} - \overset{sp}{C} \equiv \overset{sp}{CH}$

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Only 36 foreign students register for JEE Advanced

Despite holding a good ground in global rankings, IITs have failed to catch the fancy of international aspirants this year.

Only 36 candidates have registered for JEE (Advanced)—the entry level test for admission to IITs—this year as against 69 last year. Eventually, only 31 this year appeared for the test last year and seven qualified.

Not just the rankings, IITs, on their own, have been taking mindful efforts in the last few years to increase students' diversity on campus. Only last year, the premier institutes decided to reach out to international students in Sri Lanka, Nepal, Singapore, Bangladesh, Ethiopia and the UAE, and have been holding exams at these centres.

"We have been releasing admission details from time to time on our website and are also taking all measures to promote the institutes in these countries. We approach the Indian embassies in the selected countries with all the admission data required to ensure a smooth conduct of the test," said an official from the JEE (advanced) committee.

However, the efforts are not translating into numbers for the country's elite group of institutes. "Our country has to offer good liveable conditions, safety and security, better social conditions to international students to make it a lucrative destination. Why do our students prefer studying in the western part of Europe and not eastern Europe? Why do we prefer going to Northern America instead of south. It is the same case here. People look at options to study abroad also for a prospective career destination. Holding exams in select countries may not yield desirable results," said a professor.

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10 MIND BLOWING OLYMPIAD PROBLEMS

OBJECTIVE PROBLEMS

1. Relative decrease in vapour pressure of an aqueous solution containing 2 mol of $[Cu(NH_3)_3Cl]Cl$ in 3 mol H_2O is $\frac{1}{2}$. When the given solution reacts with excess of $AgNO_3$ solution, the number of moles of AgCl produced is
   (a) 1 (b) 0.25 (c) 2 (d) 0.40

2. For $NH_2OH{\cdot}HCl + NaNO_2 \longrightarrow (A) \xrightarrow{Cu} (B) + (X)_g$, which of the following is correct?
   (a) (*B*) is an amphoteric oxide.
   (b) (*X*) is a colourless, diamagnetic gas which combines with Al on heating.
   (c) (*X*) can be produced by action of (Zn + NaOH) on $NaNO_2$.
   (d) None of these

3. A 5.0 g mixture of lead nitrate and sodium nitrate was heated below 600 °C until the mass of the residue was constant. If the loss of mass is 28%, find the mass of sodium nitrate in the original mixture. (Pb = 207 u ; N = 14 u ; O = 16 u ; Na = 23 u)
   (a) 3.32 g (b) 1.68 g
   (c) 1.92 g (d) 3.6 g

4. Which statement about the composition of the vapour over an ideal 1 : 1 molal mixture of benzene and toluene is correct? (T = 25°C)

Compound	Vapour pressure data
Benzene	75 mmHg
Toluene	22 mmHg

   (a) Vapour will contain a higher number of benzene.
   (b) Vapour will contain a higher percentage of toluene.
   (c) Vapour will contain equal amounts of benzene and toluene.
   (d) Not enough information is given to make a prediction. *(US Olympiad)*

5. $\underset{\text{Salicylic acid}}{C_7H_6O_3} + \underset{\text{Acetic anhydride}}{C_4H_6O_3} \longrightarrow \underset{\text{Aspirin}}{C_9H_8O_4} + \underset{\text{Acetic acid}}{C_2H_4O_2}$

   What is percent yield of 0.85 g of aspirin formed in the reaction of 1 g of salicylic acid with excess of acetic anhydride?

Substance	Molar mass
$C_7H_6O_3$	135.12 g/mol
$C_4H_6O_3$	102.09 g/mol
$C_9H_8O_4$	180.15 g/mol
$C_2H_4O_2$	60.05 g/mol

   (a) 65% (b) 75%
   (c) 8% (d) 91% *(US Olympiad)*

SUBJECTIVE PROBLEMS

6. (i) An inorganic iodide (*A*) on heating with a solution of KOH gives a gas (*B*) and the solution of a compound (*C*).
   (ii) The gas (*B*) on ignition in air gives a compound (*D*) and water.
   (iii) Copper sulphate is reduced to the metal on passing (*B*) through the solution.
   (iv) A precipitate of the compound (*E*) is formed on reaction of (*C*) with copper sulphate solution.
   Identify (*A*) to (*E*) and give chemical equations for reactions at steps (i) to (iv).

7. Compound (*A*) with empirical formula C_7H_9N on diazotisation gives a product which undergoes Sandmeyer's reaction with Cu_2Cl_2 and HCl to give a compound (*B*). (*B*) on oxidation gives a compound (*C*) which when heated with soda lime gives chlorobenzene. Give the structures of (*A*), (*B*) and (*C*) and the reactions.

8. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6x litre/hour of

O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion etc. are the same for both fuels and that the gases behave ideally. Enthalpies of combustion : CH_4 = 809 kJ mol^{-1}; C_4H_{10} = 2878 kJ mol^{-1}.

9. An electrochemical cell is constructed with a piece of copper wire in a 1.00 M solution of $Cu(NO_3)_2$ and a piece of chromium wire in a 1.00 M solution of $Cr(NO_3)_3$.
The standard reduction potentials for $Cr^{3+}_{(aq)}$ and $Cu^{2+}_{(aq)}$ are :

$$Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}\ ;\ -0.744V$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}\ ;\ 0.340V$$

(a) Write a balanced equation for the spontaneous reaction that occurs in this cell and calculate the potential it produces.
(b) Sketch a diagram for this cell.
  (i) Label the anode.
  (ii) Show the direction of electron flow in the external circuit.
  (iii) Show the direction of movement of nitrate ions. Explain.
(c) The cell is allowed to operate until the $[Cu^{2+}] = 0.10$ M.
  (i) Find the $[Cr^{3+}]$.
  (ii) Calculate the cell potential at these concentrations.

(US National Chemistry Olympiad)

10. An LPG cylinder weighs 14.8 kg when empty, when full, it weighs 29.0 kg and shows a pressure of 2.5 atm. In course of use at 27 °C, the mass of full cylinder reduced to 23.2 kg. Find out the volume of gas in cubic metres used up at the normal usage conditions and the final pressure inside the cylinder.
(LPG is *n*-butane with normal boiling point 0 °C)

(NSEC)

SOLUTIONS

1. **(a) :** Let the degree of ionisation of the complex, $[Cu(NH_3)_3Cl]Cl$ be α.

$$[Cu(NH_3)_3Cl]Cl \rightleftharpoons [Cu(NH_3)_3Cl]^+ + Cl^-$$

$$i = 1 + \alpha$$

$$\frac{\Delta p}{p^\circ} = \frac{n_1(1+\alpha)}{n_1(1+\alpha)+n_2} = \frac{2(1+\alpha)}{2(1+\alpha)+3} = \frac{1}{2}$$

$$\alpha = \frac{1}{2} \Rightarrow 50\%\ \text{dissociation}$$

Thus, 2 moles of $[Cu(NH_3)_3Cl]Cl$ will give 1 mole of Cl^- ions.
∴ 1 mole of AgCl is produced.

2. **(b) :** $NH_2OH{\cdot}HCl + NaNO_2 \longrightarrow \underset{(A)}{N_2O} \xrightarrow{Cu} \underset{(B)}{CuO} + \underset{(X)}{N_2}$

(a) CuO is a basic oxide.
(b) N_2 is a colourless, diamagnetic gas which combines with Al.

$$2Al + N_2 \longrightarrow 2AlN$$

(c) Zn + NaOH evolves H_2 which reduces $NaNO_2$ to form NH_3 gas.

$$NaNO_2 + 6[H] \longrightarrow NaOH + NH_3 + H_2O$$

3. **(b) :** Let the mass of $Pb(NO_3)_2$ in the mixture is *x* g.
∴ The mass of sodium nitrate in the mixture = (5 – *x*) g
The desired reactions are :

$$\underset{662\ g}{2Pb(NO_3)_2} \longrightarrow \underset{446\ g}{2PbO} + 4NO_2 + O_2$$

$$\underset{170\ g}{2NaNO_3} \longrightarrow \underset{138\ g}{2NaNO_2} + O_2$$

Loss of mass is 28% of 5 g = 28/100 × 5 = 1.4 g

Mass of residue left = (5 – 1.4) g = 3.6 g ... (i)
662 g lead nitrate on heating produces PbO = 446 g
x g lead nitrate on heating would produce PbO

$$= \frac{446}{662} \times x\ \text{g}$$

Similarly, 170 g $NaNO_3$ on heating produces $NaNO_2$

$$= 138\ \text{g}$$

(5.0 – *x*)g $NaNO_3$ on heating produces $NaNO_2$

$$= \frac{138}{170} \times (5-x)$$

Total residue after heating $= \frac{446}{662}x + \frac{138}{170} \times (5-x)$ ... (ii)

Equating (i) with (ii), $\frac{446}{662}x + \frac{138}{170}(5-x) = 3.6$

On solving, *x* = 3.32
Mass of lead nitrate in the mixture = 3.32 g
Mass of sodium nitrate in the mixture = (5 – 3.32)g

$$= 1.68\ \text{g}$$

4. **(a)**

5. **(a) :** 135.12 g/mol of salicylic acid produces 180.15 g/mol of aspirin.

⇒ 1 g/mol of salicylic acid produces $= \frac{180.15}{135.12} = 1.33$ g of aspirin
∴ 1.33 g of aspirin will be formed when the yield is 100%.
Thus, 0.85 g of aspirin formed when the yield is

$$1.33 \times 0.85 = 63.9\%$$

6. Gas (*B*) on ignition gives water, therefore, hydrogen is present in the gas.
An inorganic iodide with alkali (KOH) gives a gas (*B*), a hydrogen compound, so (*A*) may be NH_4I or PH_4I. As NH_3 does not reduce $CuSO_4$, therefore, the compound (*A*) is PH_4I.

(i) $\underset{(A)}{PH_4I} + KOH \longrightarrow \underset{(B)}{PH_3} + KI + \underset{(C)}{H_2O}$

(ii) $4PH_3 + 8O_2 \longrightarrow \underset{(D)}{P_4O_{10}} + 6H_2O$

(iii) $3CuSO_4 + 2PH_3 \longrightarrow \underset{\downarrow}{Cu_3P_2} + 3H_2SO_4$

$3Cu + 2P$

(iv) $2CuSO_4 + 4KI \longrightarrow \underset{(C)}{Cu_2I_2} + 2K_2SO_4 + I_2$

7. Given: $C_7H_9N \xrightarrow{\text{Diazotisation}}$ Diazotised product $\xrightarrow[HCl]{Cu_2Cl_2} \underset{(B)}{\quad} \xrightarrow{[O]} \underset{(C)}{\quad} \xrightarrow[\Delta]{\text{Soda lime}}$ Chlorobenzene

Since chlorobenzene is obtained from (*C*) on soda lime treatment, hence (*C*) is chlorobenzoic acid. As (*C*) is obtained from (*B*) on oxidation, considering molecular formula of (*A*), a $-CH_3$ group should be attached to benzene ring which gets oxidised to $-COOH$. (*B*) is obtained after diazotisation and Sandmeyer's reaction of (*A*).

Structure of *A*: $C_6H_4\begin{cases}CH_3\\NH_2\end{cases}$ (*o*-, *m*- or *p*-) toluidines

Reactions:

$$\underset{(A)}{C_6H_4\begin{cases}CH_3\\NH_2\end{cases}} \xrightarrow{\text{diazotisation}} \underset{\text{Diazotised product}}{C_6H_4\begin{cases}CH_3\\N_2Cl\end{cases}} \xrightarrow[HCl]{Cu_2Cl_2} \underset{\text{Chlorotoluene}}{\underset{(B)}{C_6H_4\begin{cases}CH_3\\Cl\end{cases}}}$$

$$\underset{(B)}{C_6H_4\begin{cases}CH_3\\Cl\end{cases}} \xrightarrow{[O]} \underset{\text{Chlorobenzoic acid}}{\underset{(C)}{C_6H_4\begin{cases}COOH\\Cl\end{cases}}} \xrightarrow[\Delta]{\text{Sodalime}} \underset{\text{Chlorobenzene}}{C_6H_5Cl}$$

8. The combustion reactions are

$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$,

$C_4H_{10(g)} + \frac{13}{2}O_{2(g)} \longrightarrow 4CO_{2(g)} + 5H_2O_{(g)}$

Calorific value of $CH_4 = \frac{809}{16}$ kJ g^{-1}

Calorific value of $C_4H_{10} = \frac{2878}{58}$ kJ g^{-1}

Mass of C_4H_{10} having the same calorific output as that of $CH_4 = \frac{809}{16} \times \frac{58}{2878}$ g

Amount of C_4H_{10} having the same calorific output as that of $CH_4 = \frac{809}{16 \times 2878}$ mol

Now, $\frac{1}{16}$ mol CH_4 requires the supply x L/h of CH_4

$\frac{809}{16 \times 2878}$ mol C_4H_{10} requires the supply of

$\frac{x}{1/16} \times \frac{809}{16 \times 2878} = 0.28x$ L/h of C_4H_{10}

The corresponding supply of O_2

$= 0.28x \times 3 \times \frac{13}{2} = 5.48\ x$ L/h

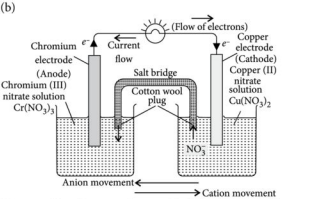
9. The balanced equation for the spontaneous reaction is

(a) $2Cr_{(s)} + 3Cu^{2+}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3Cu_{(s)}$

$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Cr^{3+}/Cr}$

$= 0.340\ V - (-0.744)\ V = 1.084\ V$

(b)



Electrons flow from anode to cathode in the external circuit. Anions (NO_3^-) move away from cathode, where they are present in excess, towards anode, where they are needed to balance the charge of the cations formed, through salt bridge.

(c) (i) $[Cu^{2+}]$ goes from 1.0 M to 0.10 M, so

$\Delta[Cu^{2+}] = -0.90$; $\Delta[Cr^{3+}] = 0.90 \times 2/3 = 0.60$

So, $[Cr^{3+}] = 1 + 0.6 = 1.60$

(ii) Put these values into the following equation :

$$E = E^\circ - \frac{RT}{nF}\log\frac{\left[Cr^{3+}\right]^2}{\left[Cu^{2+}\right]^3}$$

$$E = 1.084 - \frac{0.0591}{6}\log\frac{(1.60)^2}{(0.10)^3} = 1.084 - 0.033 = 1.051\ V$$

10. (a) : Weight of LPG originally present = 29 – 14.8 = 14.2 kg

Weight of LPG present after use = 23.2 – 14.8 = 8.4 kg

Weight of used gas = 14.2 – 8.4 = 5.8 kg

Moles of gas $= \frac{5.8 \times 10^3}{58} = 100$ mol

At normal conditions, $P = 1$ atm, $T = 273 + 27 = 300$ K

As, $V = \frac{nRT}{P} = \frac{100 \times 0.082 \times 300}{1} = 2463\ dm^3$

$\therefore \quad V = 2.463\ cm^3$

Since, volume is constant. $PV = nRT$, pressure = 2.5 atm

$$\frac{P_1}{P_2} = \frac{n_1}{n_2} = \frac{w_1/M}{w_2/M} = \frac{w_1}{w_2} \Rightarrow \frac{2.5}{P_2} = \frac{14.2}{8.4}$$

$\Rightarrow P_2 = \frac{2.5 \times 8.4}{14.2} = 1.48$ atm

JEE MAIN

Online 15th April (Morning)

SOLVED PAPER 2018

GOOD NEWS

We are happy to inform our readers that most of the questions asked in JEE Main 2018 Exam are similar to the problems given in **MTG JEE Books.**

GOOD NEWS

1. In the molecular orbital diagram for the molecular ion, N_2^+, the number of electrons in the σ_{2p} molecular orbital is

(a) 3 (b) 1 (c) 0 (d) 2

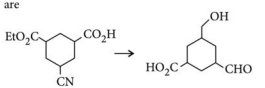
2. An ideal gas undergoes a cyclic process as shown in figure :

$\Delta U_{BC} = -5$ kJ mol^{-1},
$q_{AB} = 2$ kJ mol^{-1},
$W_{AB} = -5$ kJ mol^{-1},
$W_{CA} = 3$ kJ mol^{-1}

Heat absorbed by the system during process CA is

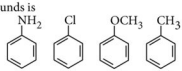
(a) 18 kJ mol^{-1} (b) +5 kJ mol^{-1}
(c) −5 kJ mol^{-1} (d) −18 kJ mol^{-1}

3. The reagent(s) required for the following conversion are



(a) (i) $LiAlH_4$, (ii) H_3O^+
(b) (i) B_2H_6, (ii) DIBAL-H, (iii) H_3O^+
(c) (i) B_2H_6, (ii) $SnCl_2$/HCl, (iii) H_3O^+
(d) (i) $NaBH_4$, (ii) Raney Ni/H_2, (iii) H_3O^+

4. The increasing order of nitration of the following compounds is



(a) $(B) < (A) < (C) < (D)$
(b) $(B) < (A) < (D) < (C)$
(c) $(A) < (B) < (C) < (D)$
(d) $(A) < (B) < (D) < (C)$

5. The decreasing order of bond angles in BF_3, NH_3, PF_3 and I_3^- is

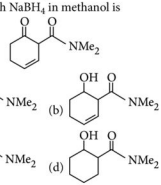
(a) $I_3^- > BF_3 > NH_3 > PF_3$
(b) $BF_3 > NH_3 > PF_3 > I_3^-$
(c) $I_3^- > NH_3 > PF_3 > BF_3$
(d) $BF_3 > I_3^- > PF_3 > NH_3$

6. $H-\overset{(I)}{N}\cdots\overset{(II)}{N}\cdots N$

In hydrogen azide (above) the bond orders of bonds (I) and (II) are

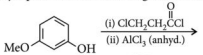
	(I)	(II)
(a)	>2	< 2
(b)	< 2	< 2
(c)	< 2	> 2
(d)	> 2	> 2

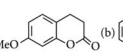
7. The main reduction product of the following compound with $NaBH_4$ in methanol is

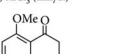


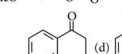
8. Identify the pair in which the geometry of the species is T-shape and square-pyramidal, respectively.
(a) IO_3^- and $IO_2F_2^-$ (b) $XeOF_2$ and $XeOF_4$
(c) ICl_2^- and ICl_5 (d) ClF_3 and IO_4^-

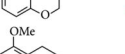
9. The major product of the following reaction is



(a) 

(b) 

(c) 

(d) 

10. The IUPAC name of the following compound is

(a) 4-methyl-3-ethylhex-4-ene
(b) 4,4-diethyl-3-methylbut-2-ene
(c) 3-ethyl-4-methylhex-4-ene
(d) 4-ethyl-3-methylhex-2-ene.

11. For which of the following reactions, ΔH is equal to ΔU ?
(a) $2NO_{2(g)} \rightarrow N_2O_{4(g)}$
(b) $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$
(c) $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$
(d) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

12. The correct combination is

(a)	$[Ni(CN)_4]^{2-}$	–	tetrahedral;
	$[Ni(CO)_4]$	–	paramagnetic
(b)	$[NiCl_4]^{2-}$	–	paramagnetic;
	$[Ni(CO)_4]$	–	tetrahedral
(c)	$[NiCl_4]^{2-}$	–	diamagnetic;
	$[Ni(CO)_4]$	–	square-planar
(d)	$[NiCl_4]^{2-}$	–	square-planar;
	$[Ni(CN)_4]^{2-}$	–	paramagnetic

13. For Na^+, Mg^{2+}, F^- and O^{2-} ; the correct order of increasing ionic radii is
(a) $Mg^{2+} < Na^+ < F^- < O^{2-}$
(b) $O^{2-} < F^- < Na^+ < Mg^{2+}$
(c) $Na^+ < Mg^{2+} < F^- < O^{2-}$
(d) $Mg^{2+} < O^{2-} < Na^+ < F^-$

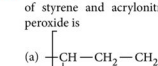
14. Xenon hexafluoride on partial hydrolysis produces compounds '*X*' and '*Y*'. Compounds '*X*' and '*Y*' and the oxidation state of Xe are respectively
(a) XeO_2F_2 (+6) and XeO_3 (+4)
(b) $XeOF_4$ (+6) and XeO_2F_2 (+6)
(c) $XeOF_4$ (+6) and XeO_3 (+6)
(d) XeO_2 (+4) and XeO_3 (+6)

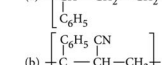
15. N_2O_5 decomposes to NO_2 and O_2 and follows first order kinetics. After 50 minutes, the pressure inside the vessel increases from 50 mmHg to 87.5 mmHg. The pressure of the gaseous mixture after 100 minutes at constant temperature will be
(a) 116.25 mmHg (b) 175.0 mmHg
(c) 106.25 mmHg (d) 136.25 mmHg.

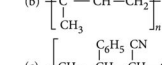
16. Ejection of the photoelectron from metal in the photoelectric effect experiment can be stopped by applying 0.5 V when the radiation of 250 nm is used. The work function of the metal is
(a) 5 eV (b) 4 eV (c) 5.5 eV (d) 4.5 eV

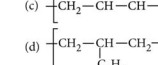
17. A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the aforementioned solution, a white precipitate is obtained which does not dissolve in dil. nitric acid. The anion is
(a) S^{2-} (b) SO_4^{2-} (c) CO_3^{2-} (d) Cl^-

18. The copolymer formed by addition polymerization of styrene and acrylonitrile in the presence of peroxide is

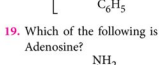
(a) 

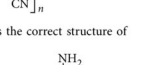
(b) 

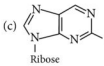
(c) 

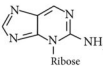
(d) 

19. Which of the following is the correct structure of Adenosine?

(a) 

(b) 

(c) 

(d) 

20. In which of the following reactions, an increase in the volume of the container will favour the formation of products?

(a) $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$

(b) $3O_{2(g)} \rightleftharpoons 2O_{3(g)}$

(c) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

(d) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(l)}$

21. The correct match between items of List-I and List-II is

List-I		List-II	
A.	Coloured impurity	P.	Steam distillation
B.	Mixture of *o*-nitrophenol and *p*-nitrophenol	Q.	Fractional distillation
C.	Crude Naphtha	R.	Charcoal treatment
D.	Mixture of glycerol and sugars	S.	Distillation under reduced pressure

(a) (A)-(R), (B)-(S), (C)-(P), (D)-(Q)

(b) (A)-(R), (B)-(P), (C)-(Q), (D)-(S)

(c) (A)-(P), (B)-(S), (C)-(R), (D)-(Q)

(d) (A)-(R), (B)-(P), (C)-(S), (D)-(Q)

22. The minimum volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$; atomic mass of Pb = 207 u) is

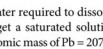
(a) 0.36 L (b) 0.18 L (c) 17.98 L (d) 1.798 L

23. Which of the following will not exist in zwitter ionic form at pH = 7 ?

(a) 

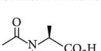
(b) 

(c) 

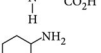
(d) 

24. Which of the following will most readily give the dehydrohalogenation product?

(a) 

(b) 

(c) 

(d) 

25. A sample of $NaClO_3$ is converted by heat to NaCl with a loss of 0.16 g of oxygen. The residue is dissolved in water and precipitated as AgCl. The mass of AgCl (in g) obtained will be

(Given : Molar mass of AgCl = 143.5 g mol^{-1})

(a) 0.54 (b) 0.35 (c) 0.48 (d) 0.41

26. Which of the following statements about colloids is false?

(a) When excess of electrolyte is added to colloidal solution, colloidal particle will be precipitated.

(b) Freezing point of colloidal solution is lower than true solution at same concentration of a solute.

(c) When silver nitrate solution is added to potassium iodide solution, a negatively charged colloidal solution is formed.

(d) Colloidal particles can pass through ordinary filter paper.

27. In graphite and diamond, the percentage of *p*-characters of the hybrid orbitals in hybridisation are respectively

(a) 33 and 75 (b) 50 and 75

(c) 33 and 25 (d) 67 and 75

28. Which of the following arrangements shows the schematic alignment of magnetic moments of antiferromagnetic substance?

(a) ↑ ↓ ↓ ↓ ↓ ↑

(b) ↑ ↑ ↑ ↑ ↑ ↑

(c) ↑ ↑ ↓ ↑ ↑ ↓

(d) ↑ ↓ ↑ ↓ ↑ ↓

29. When an electric current is passed through acidified water, 112 mL of hydrogen gas at N.T.P. was collected at the cathode in 965 seconds. The current passed, in ampere, is

(a) 2.0 (b) 1.0 (c) 0.1 (d) 0.5

30. Which of the following is a Lewis acid?

(a) NaH (b) NF_3 (c) PH_3 (d) $B(CH_3)_3$

SOLUTIONS

1. (b): Molecular orbital electronic configuration of N_2^+ : $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_y^2 = \pi 2p_z^2\ \sigma 2p_x^1$

Therefore, the number of electrons in $\sigma 2p_x$ M.O. = 1

2. (b): From the first law of thermodynamics :

$\Delta U = q + w$

Where, q = Heat change

w = work done

Now, for state $A \rightarrow B$,

$\Delta U_{AB} = q_{AB} + w_{AB} = 2 - 5 = -3$ kJ mol^{-1}

For state $A \rightarrow B \rightarrow C$,

$\Delta U_{ABC} = \Delta U_{AB} + \Delta U_{BC} = -3 - 5 = -8$ kJ mol^{-1}

$\Delta U_{CBA} = -\Delta U_{ABC} = -(-8) = +8$ kJ mol^{-1}

As, internal energy is a state function, thus,

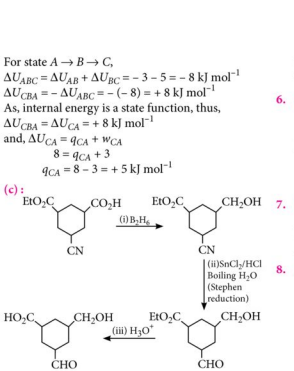
$\Delta U_{CBA} = \Delta U_{CA} = +8$ kJ mol^{-1}

and, $\Delta U_{CA} = q_{CA} + w_{CA}$

$8 = q_{CA} + 3$

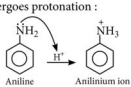
$q_{CA} = 8 - 3 = +5$ kJ mol^{-1}

3. (c) :



4. (d): Nitration is an electrophilic substitution reaction. Thus, groups which increase the electron density on benzene ring will have greater ease for nitration.

$-OCH_3$ group shows $+R$ effect but $-CH_3$ group shows inductive effect ($+I$). $-Cl$ will have strong electron withdrawing effect ($-I$). In acidic medium, aniline undergoes protonation :



Thus, electron density on the benzene ring will be least in aniline. Therefore, aniline is least reactive.

Thus, increasing order of nitration is,

$(A) < (B) < (D) < (C)$.

5. (a) :

Species	Bond angle
BF_3	120°
NH_3	107°
PF_3	100°
I_3^-	180°

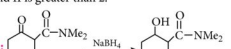
BF_3 is trigonal planar (sp^2 hybridised). NH_3 is pyramidal (sp^3 hybridised) with one lone pair. PF_3 is also pyramidal but its bond angle is lesser than NH_3 due to lesser bond pair repulsions than NH_3 as fluorine is more electronegative than hydrogen, the electron pairs are attracted more towards F, giving lesser repulsion between bond pairs in PF_3. I_3^- has linear shape.

6. (c) : The structure of hydrogen azide is

$$H-\overset{(I)}{N}=\overset{(II)}{N}\equiv N$$

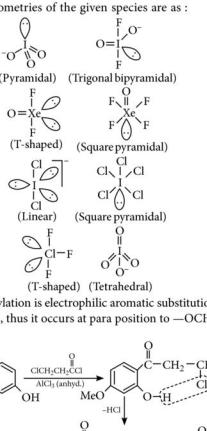
Bond order of bond I is less than 2. Bond order of bond II is greater than 2.

7. (b):

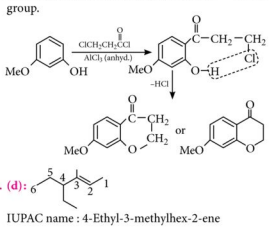


$NaBH_4$ does not reduce double bonds and amide groups.

8. (b): Geometries of the given species are as :



9. (c) : Acylation is electrophilic aromatic substitution reaction, thus it occurs at para position to $-OCH_3$ group.



10. (d):

IUPAC name : 4-Ethyl-3-methylhex-2-ene

11. (b): $\Delta H = \Delta U + \Delta n_g RT$

ΔH will be equal to ΔU if , Δn_g is zero, *i.e.*, moles of gaseous reactants and products are equal.

a. $2NO_{2(g)} \rightarrow N_2O_{4(g)}$; $\Delta n_g = 1 - 2 = -1$

b. $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$; $\Delta n_g = (1 + 1) - 2 = 0$

c. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$

$\Delta n_g = 2 - (2 + 1) = -1$

d. $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$; $\Delta n_g = 2 - (1 + 3) = -2$

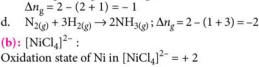
12. (b): $[NiCl_4]^{2-}$:

Oxidation state of Ni in $[NiCl_4]^{2-} = +2$

Ni^{2+} : [Ar] 

Cl^- is a weak field ligand and cannot take part in pairing of electrons.

$[NiCl_4]^{2-}$:

[Ar] 

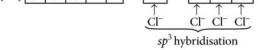
Hence, the complex is tetrahedral and paramagnetic with two unpaired electrons.

$[Ni(CN)_4]^{2-}$:

Oxidation state of Ni in $[Ni(CN)_4]^{2-} = +2$

CN^- is a strong field ligand, thus pairing of electrons takes place in *d*-orbitals.

$[Ni(CN)_4]^{2-}$:

[Ar] 

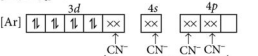
Hence, the complex is square planar and diamagnetic.

$[Ni(CO)_4]$:

Oxidation state of Ni in $[Ni(CO)_4]$ is zero. CO is a strong field ligand.

Ni : [Ar] 

$[Ni(CO)_4]$:

[Ar] 

Hence, the complex is tetrahedral and diamagnetic.

13. (a): Na^+, Mg^{2+}, F^- and O^{2-} are isoelectronic species. For isoelectronic species, the ionic radius increases with increase in negative charge and decreases with increase in positive charge. Thus, increasing order of ionic radii is :

$Mg^{2+} < Na^+ < F^- < O^{2-}$

14. (b): Partial hydrolysis of XeF_6 gives $XeOF_4(X)$ and $XeO_2F_2(Y)$:

$XeF_6 + H_2O \rightarrow \underset{(X)}{XeOF_4} + 2HF$

$XeF_6 + 2H_2O \rightarrow \underset{(Y)}{XeO_2F_2} + 4HF$

Let, oxidation states of Xe in $XeOF_4$ and XeO_2F_2 be *a* and *b* respectively.

$XeOF_4$:

$a + (-2) + 4 \times (-1) = 0 \Rightarrow a = +6$

XeO_2F_2 :

$b + 2 \times (-2) + 2 \times (-1) = 0 \Rightarrow b = +6$

15. (c):

	N_2O_5	$\rightleftharpoons$	$2NO_2$	+	$1/2\ O_2$
At $t = 0$	50 mm Hg		0		0
At $t = 50$ min	$50 - p_1$		$2p_1$		$\frac{p_1}{2}$

Total pressure at $t = 50$ min is

$50 - p_1 + 2p_1 + \frac{p_1}{2} = 87.5$ mmHg

$50 + 1.5\ p_1 = 87.5$

$p_1 = \frac{37.5}{1.5} = 25$ mmHg

Since, $t = 50$ min. is the half- life period for the reaction.

Thus, $t = 100$ min. is equal to two half-lives.

	N_2O_5	$\rightleftharpoons$	$2NO_2$	+	$\frac{1}{2}O_2$
$t = 100$ min	$50 - p_2$		$2p_2$		$\frac{p_2}{2}$

$\therefore \quad 50 - p_2 = \frac{25}{2}$ (At 2^{nd} half life)

$p_2 = 37.5$ mmHg

Total pressure at $t = 100$ min $= 50 - p_2 + 2p_2 + \frac{p_2}{2}$

$= 50 + 1.5\ p_2 = 50 + 1.5 \times 37.5 = 106.25$ mmHg

16. (d): $K.E. = h\upsilon - h\upsilon_0 = E - W_0$

where, *K.E.* = Kinetic energy of ejected electron = stopping potential

E = Energy absorbed

W_0 = Work function

$E = h\upsilon = \frac{hc}{\lambda}$

$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{250 \times 10^{-9}} = 7.9512 \times 10^{-19}\ J = 4.96\ eV$

Then, $0.5 = 4.96 + W_0$

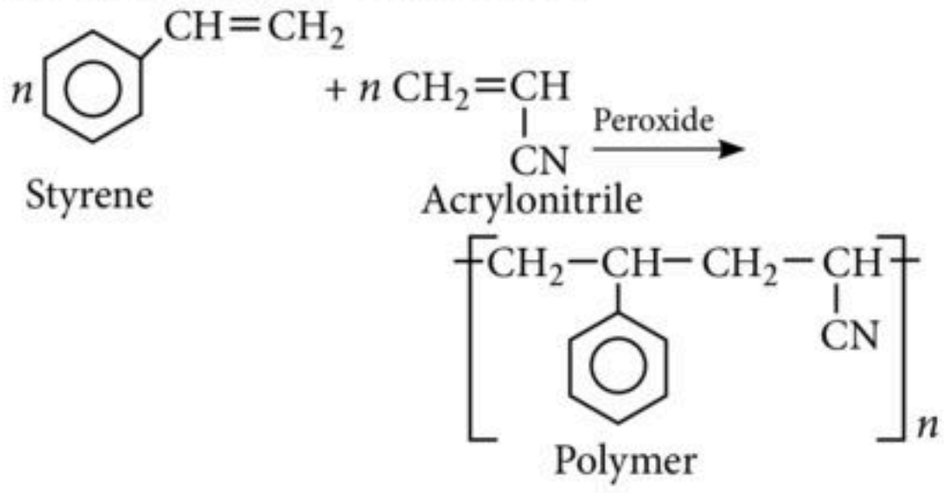
$W_0 = 4.46 \approx 4.5$ eV

17. (d): The anion is Cl^-. Sodium salt of Cl^-, *i.e.*, NaCl is neutral to litmus.

$$NaCl + AgNO_3 \rightarrow \underset{\text{White ppt.}}{AgCl\downarrow} + NaNO_3$$

AgCl does not dissolve in dil. nitric acid.

18. (d): Polymerisation of styrene with acrylonitrile occurs in presence of peroxide.



19. (a)

20. (a): According to Boyle's law :

$$\text{Pressure} \propto \frac{1}{\text{Volume}}$$

i.e., when volume of the container is increased, the pressure decreases. To undo the effect of decreased pressure, the reaction will move in a direction where pressure increases *i.e.*, towards the greater number of moles of gaseous substances. This is in accordance with Le-Chatelier's principle.

21. (b)

22. (b): $PbCl_2 \rightleftharpoons \underset{s}{Pb^{2+}} + \underset{2s}{2Cl^-}$

(s = solubility of $PbCl_2$)

$K_{sp} = [Pb^{2+}]\,[Cl^-]^2$

$3.2 \times 10^{-8} = s \times (2s)^2 = 4s^3$

$s = 2 \times 10^{-3}$ M

$$\text{Solubility} = \frac{n_{PbCl_2}}{\text{Volume (in L)}}$$

$$s = \frac{0.1}{278} \times \frac{1}{V} = 2 \times 10^{-3}$$

$$V = \frac{0.1}{278} \times \frac{10^3}{2} = 0.1798 \simeq 0.18 \text{ L}$$

23. (b): The dipolar structure of amino acid is called zwitter ion. In structure (b), the nitrogen atom is not basic as it is an amide nitrogen. Thus, it cannot form zwitter ion.

24. (c)

25. (c) : Decomposition of $NaClO_3$ is given as :

$$\underset{\text{(Residue)}\quad 0.16\text{ g}}{2NaClO_3} \xrightarrow{\Delta} 2NaCl + 3O_2$$

No. of moles of O_2 formed $= \frac{0.16}{32} = 5 \times 10^{-3}$

$$n_{NaCl} = \frac{2}{3} n_{O_2} = \frac{2}{3} \times 5 \times 10^{-3} = \frac{1}{300}$$

$NaCl + Ag^+ \rightarrow AgCl + Na^+$

1 mole of AgCl is precipitated from one mole of NaCl.

$\therefore$ Mole of AgCl $= \frac{1}{300}$

$\therefore$ Mass of AgCl = Molar mass of AgCl $\times\, n_{AgCl}$

$$= 143.5 \times \frac{1}{300} \simeq 0.48 \text{ g}$$

26. (b): Freezing point of colloidal solution is higher than true solution at the same concentration of a solute.

27. (d): The hybridisation of carbon in graphite is sp^2.

$$\%\ p\text{-character} = \frac{2}{3} \times 100 = 67\%$$

The hybridisation of carbon in diamond is sp^3.

$$\therefore \quad \%\ of\ p\text{-character} = \frac{3}{4} \times 100 = 75\%$$

28. (d): In antiferromagnetic substances, the magnetic dipoles are oppositely oriented and cancel out each other's magnetic moment.

29. (b): $2H^+ + 2e^- \rightarrow H_2$ (at cathode)

$$w = ZIt = \frac{EIt}{96500}$$

$$\text{Moles of } H_2 \text{ deposited} = \frac{112}{22400}$$

Mass of H_2 deposited (w) = Moles $\times$ Molar mass

$$= \frac{112}{22400} \times 2$$

$$\text{Thus, } \frac{112}{22400} \times 2 = \frac{1 \times I \times 965}{96500} \quad \Rightarrow \quad I = 1 \text{ A}$$

30. (d)

Quotable Quote

The important thing is not to stop questioning. Curosity has its own reason for existence. One cannot help but be in awe when he contemplates the mysteries of eternity, of life, of the marvelous structure of reality. It is enough if one tries merely to comprehend a little to this mystery each day.

Albert Einstein

SOLVED PAPER **2018**

Karnataka CET

1. 1.0 g of Mg is burnt with 0.28 g of O_2 in a closed vessel. Which reactant is left in excess and how much?
(a) Mg, 5.8 g (b) Mg, 0.58 g
(c) O_2, 0.24 g (d) O_2, 2.4 g

2. The orbital nearest to the nucleus is
(a) *4f* (b) *5d* (c) *4s* (d) *7p*.

3. Which of the following is the correct order of radius?
(a) $H^- > H > H^+$ (b) $Na^+ > F^- > O^{2-}$
(c) $F^- > O^{2-} > Na^+$ (d) $Al^{3+} > Mg^{2+} > Mn^{3-}$

4. The intramolecular hydrogen bond is present in
(a) phenol (b) *o*-nitrophenol
(c) *p*-nitrophenol (d) *p*-cresol.

5. The state of hybrid orbitals of carbon in CO_2, CH_4 and CO_3^{2-} respectively is
(a) sp^3, sp^2 and *sp* (b) sp^3, *sp* and sp^2
(c) *sp*, sp^3 and sp^2 (d) sp^2, sp^3 and *sp*.

6. For an ideal gas, compressibility factor is
(a) 0 (b) 1 (c) –1 (d) +2

7. The relationship between K_p and K_c is $K_p = K_c(RT)^{\Delta n}$. What would be the value of Δn for the reaction.
$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$?
(a) 1 (b) 0.5 (c) 1.5 (d) 2

8. Acidity of BF_3 can be explained on which of the following concepts?
(a) Arrhenius concept
(b) Bronsted Lowry concept
(c) Lewis concept
(d) Bronsted Lowry as well as Lewis concept.

9. For the redox reaction,
$xMnO_4^- + yH_2C_2O_4 + zH^+ \rightarrow mMn^{2+} + nCO_2 + pH_2O$.
The values of *x*, *y*, *m* and *n* are
(a) 10, 2, 5, 2 (b) 2, 5, 2, 10
(c) 6, 4, 2, 4 (d) 3, 5, 2, 10

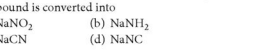
10. H_2O_2 is
(a) an oxidising agent
(b) a reducing agent
(c) both oxidising and reducing agent
(d) neither oxidising nor reducing agent.

11. Dead burnt plaster is
(a) $CaSO_4$ (b) $CaSO_4 \cdot \frac{1}{2}H_2O$
(c) $CaSO_4 \cdot H_2O$ (d) $CaSO_4 \cdot 2H_2O$

12. Identify the following compound which exhibits geometrical isomerism.
(a) But-2-ene (b) But-1-ene
(c) Butane (d) *Iso*-butane

13. During the fusion of organic compound with sodium metal, nitrogen present in the organic compound is converted into
(a) $NaNO_2$ (b) $NaNH_2$
(c) NaCN (d) NaNC

14. The reagent '*X*' used for the following reaction is



(a) Ni (b) Pd/C
(c) $LiAlH_4$ (d) Na/liquid NH_3

15. Which of the following ions will cause hardness in water?
(a) Ca^{2+} (b) Na^+ (c) Cl^- (d) K^+

16. Which of the following oxides show electrical properties like metals?
(a) SiO_2 (b) MgO (c) $SO_{2(s)}$ (d) CrO_2

17. Which of the following aqueous solutions should have the highest boiling point?

(a) 1.0 M NaOH (b) 1.0 M Na_2SO_4
(c) 1.0 M NH_2NO_3 (d) 1.0 M KNO_3

18. The charge required for the reduction of 1 mole of MnO_4^- to MnO_2 is
(a) 1 F (b) 3 F (c) 5 F (d) 7 F

19. For the reaction, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the rate of disappearance of O_2 is 2×10^{-4} mol L^{-1} s^{-1}. The rate of appearance of SO_3 is
(a) 2×10^{-4} mol L^{-1} s^{-1}
(b) 4×10^{-4} mol L^{-1} s^{-1}
(c) 1×10^{-1} mol L^{-1} s^{-1}
(d) 6×10^{-4} mol L^{-1} s^{-1}

20. Which of the following electrolytes will have maximum coagulating value for AgI/Ag^+ sol?
(a) Na_2S (b) Na_3PO_4
(c) Na_2SO_4 (d) NaCl

21. Electrolytic refining is used to purify which of the following metals?
(a) Cu and Zn (b) Ge and Si
(c) Zr and Ti (d) Zn and Hg

22. Dry ice is
(a) solid CO (b) solid SO_2
(c) solid CO_2 (d) solid O_2.

23. Which of the following is an amphoteric oxide?
(a) V_2O_5, Cr_2O_3 (b) Mn_2O_7, Cr_2O_3
(c) CrO, V_2O_5 (d) V_2O_5, V_2O_4

24. The IUPAC name of $[Co(NH_3)_4Cl(NO_2)]Cl$ is
(a) tetraaminechloridonitrito-N-cobalt(III) chloride
(b) tetraaminechloridonitriocobalt(II) chloride
(c) tetraaminechloridonitriocobalt(I) chloride
(d) tetraaminechloridonitrocobalt(III) chloride.

25. Which of the following statements is true in case of alkyl halides?
(a) They are polar in nature.
(b) They can form hydrogen bonds.
(c) They are highly soluble in water.
(d) They undergo addition reactions.

26. Phenol can be distinguished from ethanol by the reagent
(a) bromine water (b) sodium metal
(c) iron metal (d) chlorine water.

27. Which of the following compounds undergo haloform reaction?
(a) CH_3COCH_3 (b) HCHO
(c) CH_3CH_2Br (d) $CH_3 - O - CH_3$

28. Which of the following will be the most stable diazonium salt ($RN_2^+X^-$)?
(a) $CH_3N_2^+X^-$ (b) $C_6H_5N_2^+X^-$
(c) $CH_3CH_2N_2^+X^-$ (d) $C_6H_5CH_2N_2^+X^-$

29. Which of the following bases is not present in DNA?
(a) Adenine (b) Guanine
(c) Cytosine (d) Uracil

30. Which one of the following is a polyamide polymer?
(a) Terylene (b) Nylon-6,6
(c) Buna-S (d) Bakelite

31. In *f.c.c.* the unit cell is shared equally by how many unit cell?
(a) 10 (b) 8 (c) 6 (d) 2

32. At a particular temperature, the ratio of molar conductance to specific conductance of 0.01 M NaCl solution is
(a) 10^5 cm^3 mol^{-1} (b) 10^3 cm^3 mol^{-1}
(c) 10 cm^3 mol^{-1} (d) 10^5 cm^2 mol^{-1}.

33. Isotonic solutions are having the same
(a) surface tension (b) vapour pressure
(c) osmotic pressure (d) viscosity.

34. The temperature coefficient of a reaction is 2. When the temperature is increased from 30 °C to 90 °C, the rate of reaction is increased by
(a) 150 times (b) 410 times
(c) 72 times (d) 64 times

35. Gold sol is not a
(a) lyophobic sol
(b) negatively charged sol
(c) macromolecular sol
(d) multimolecular colloid.

36. The common impurity present in bauxite is
(a) CuO (b) ZnO
(c) Fe_2O_3 (d) Cr_2O_3

37. Very pure N_2 can be obtained by
(a) thermal decomposition of ammonium dichromate
(b) treating aqueous solution of NH_4Cl and $NaNO_2$
(c) liquefaction and fractional distillation of liquid air
(d) thermal decomposition of sodium azide.

38. Which of the following oxidation states is common for all lanthanides?
(a) +2 (b) +3 (c) +4 (d) +5

39. The electronic configuration of transition element *X*, is +3, oxidation state is $[Ar]3d^5$. What is its atomic number?
(a) 25 (b) 26 (c) 27 (d) 24

40. *n*-Propyl chloride reacts with sodium metal in dry ether to give
(a) $CH_3—CH_2—CH_2—CH_2—CH_3$
(b) $CH_3—CH_2—CH_3$
(c) $CH_3—CH_2—CH_2—CH_3$
(d) $CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$

41. When the vapours of tertiary butyl alcohol are passed through heated copper at 573 K, the product formed is
(a) but-2-ene (b) 2-butanone
(c) 2-methyl propene (d) butanal.

42. What is the increasing order of acidic strength among the following?
(i) *p*-methoxy phenol (ii) *p*-methyl phenol
(iii) *p*-nitrophenol
(a) ii < iii < i (b) iii < ii < i
(c) i < ii < iii (d) i < iii < ii

43. Which of the following is more basic than aniline?
(a) Diphenylamine (b) Triphenylamine
(c) *p*-Nitroaniline (d) Benzylamine

44. The two forms of *D*-glucopyranose are called
(a) diastereomers (b) anomers
(c) epimers (d) enantiomers.

45. Among the following, the branched chain polymer is
(a) polyvinyl chloride
(b) bakelite
(c) low density polythene
(d) high density polythene.

46. Edge length of a cube is 300 pm. Its body diagonal would be
(a) 600 pm (b) 423 pm
(c) 519.6 pm (d) 450.5 pm

47. Which of the following is not a conductor of electricity?
(a) Solid NaCl (b) Cu
(c) Fused NaCl (d) Brine solution

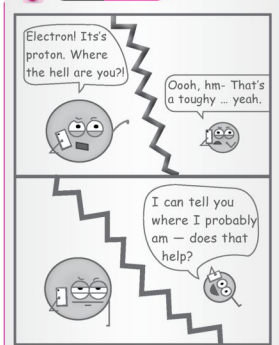
48. For a cell involving two electron changes, $E^\circ_{cell} = 0.3$ V at 25°C. The equilibrium constant of the reaction is
(a) 10^{-10} (b) 3×10^{-2}
(c) 10 (d) 10^{10}

49. The value of rate constant of pseudo first order reaction
(a) depends only on temperature
(b) depends on the concentration of reactants present in small amounts
(c) depends on the concentration of reactants present in excess
(d) is independent of the concentration of reactants.

50. $(CH_3)_3SiCl$ is used duing polymerisation of organosilicons because
(a) the chain length of organosilicon polymers can be controlled by adding $(CH_3)_3SiCl$
(b) $(CH_3)_3SiCl$ improves the quality and yield of the polymer
(c) $(CH_3)_3SiCl$ does not block the end terminal of silicone polymer
(d) $(CH_3)_3SiCl$ acts as a catalyst during polymerisation.

51. When PbO_2 reacts with concentrated HNO_3, the gas evolved is
(a) NO_2 (b) O_2
(c) N_2 (d) N_2O

COMIC CAPSULE

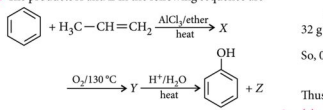


52. $KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to
(a) I_2 (b) IO^- (c) IO_3^- (d) IO_4^-

53. $[Fe(NO_2)_3Cl_3]$ and $[Fe(O-NO)_3Cl_3]$ shows
(a) linkage isomerism (b) geometrical isomerism
(c) optical isomerism (d) hydrate isomerism.

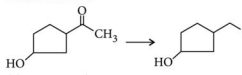
54. Tertiary alkyl halide is practically inert to substitution by S_N2 mechanism because of
(a) insolubility (b) instability
(c) inductive effect (d) steric hindrance.

55. The products *X* and *Z* in the following sequence are



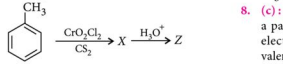
(a) *iso*-propyl benzene and acetone
(b) cumene peroxide and acetone
(c) *iso*-propyl benzene and *iso*-propyl alcohol
(d) phenol and acetone.

56. The appropriate reagent for the following transformation is



(a) Zn-Hg/HCl
(b) H_2N-NH_2, KOH/ethylene glycol
(c) Ni/H_2 (d) $NaBH_4$

57. In the following reaction,



the compound *Z* is
(a) benzoic acid (b) benzaldehyde
(c) acetophenone (d) benzene.

58. The reaction of benzenediazonium chloride with aniline yields yellow dye. The name of the yellow dye is
(a) *p*-hydroxyazobenzene
(b) *p*-aminoazobenzene
(c) *p*-nitroazobenzene
(d) *o*-nitroazobenzene.

59. The glycosidic linkage involved in linking the glucose units in amylase part of starch is
(a) C_1 - C_4 β-linkage (b) C_1 - C_6 α-linkage
(c) C_1 - C_6 β-linkage (d) C_1 - C_4 α-linkage.

60. Ziegler-Natta catalyst is used to prepare
(a) low-density polythene
(b) teflon
(c) high-density polythene
(d) nylon-6.

SOLUTIONS

1. **(b):** Balanced reaction can be given as

$$\underset{24\times2=48}{2Mg} + \underset{32}{O_2} \rightarrow 2MgO$$

32 g of O_2 is required to burn 48 g Mg

So, 0.28 g O_2 will be required for $\frac{48}{32}\times0.28$ g Mg

$= 0.42$ g of Mg

Thus, Mg will remain in excess $= 1 - 0.42 = 0.58$ g

2. **(c)** **3.** **(a)** **4.** **(b)**

5. **(c):**

6. **(b):** Compressibility factor, $Z = \frac{PV}{RT}$

For ideal gas, $PV = nRT$

So, $Z = 1$.

7. **(d):** $K_p = K_c (RT)^{\Delta n_g}$

Δn_g = sum of the stoichiometric coefficient of gaseous products – sum of stoichiometric coefficients of gaseous reactants

$\Delta n_g = 2 - 0 = 2$

8. **(c):** According to Lewis concept, acid can accept a pair of electrons and base can donate a pair of electrons. Thus, as BF_3 has six electrons in its valence shell, so it can accept an electrons pair and acts as Lewis acid.

9. **(b):** The balanced reaction is given as

$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Thus, $x = 2$, $y = 5$, $m = 2$ and $n = 10$

10. **(c):** H_2O_2 can acts both oxidising and reducing agent. Oxidising nature of H_2O_2 can be interpreted on account of the possession of labile oxygen atom.

$$H_2O_2 \rightarrow H_2O + O$$

Reducing behaviour is as

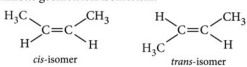
$$H_2O_2 + O \rightarrow H_2O + O_2$$

11. (a): Anhydrous calcium sulphate is known as dead burnt plaster.

12. (a): The necessary and sufficient condition for a compound to exhibit geometrical isomerism is that the two groups attached to the same carbon must be different, *i.e.*, alkenes of the following types show *cis-trans* isomerism.

abC = *Cab*, *abC* = *Ccd*, *abC* = *Cax*, *abC* = *Cbx*

Thus, out of the given examples, only but-2-ene exhibits geometrical isomerism.



cis-isomer *trans*-isomer

13. (c): The carbon and nitrogen present in an organic compound during fusion with sodium metal give sodium cyanide (NaCN).

14. (b): *cis*-Alkene is obtained by using Pd/C as a catalyst.

15. (a): The hardness of natural water is generally caused by presence of the bicarbonates chlorides and sulphates of calcium and magnesium.

16. (d): CrO_2 is a typical metal oxide which shows electrical conductivity similar to metal.

17. (b): $\Delta T_b = iK_b m$

Concentration is same for all the solutions. So,

$$\Delta T_b \propto i$$

$i = 2$ for NaOH ; $i = 3$ for Na_2SO_4

$i = 2$ for NH_4NO_3 ; $i = 2$ for KNO_3

So, elevation in boiling point will be maximum in Na_2SO_4 solution or Na_2SO_4 solution will have highest boiling point.

18. (b): $\overset{+7}{MnO_4^-} + 3e^- \longrightarrow \overset{+4}{MnO_2}$

3F charge will be required to refuse 1 mole of MnO_4^- to MnO_2.

19. (b): $2SO_2 + O_2 \rightleftharpoons 2SO_3$

$$\text{Rate of reaction} = -\frac{1}{2}\frac{d[SO_2]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[SO_3]}{dt}$$

$$2\times10^{-4} = \frac{1}{2}\frac{d[SO_3]}{dt}$$

$$\frac{d[SO_3]}{dt} = 2\times2\times10^{-4} = 4\times10^{-4} \text{ mol } L^{-1} s^{-1}$$

20. (d): The coagulation value decreases with increase in charge of the coagulating ion.

$$\text{Coagulating power} \propto \frac{1}{\text{coagulation value}} \propto \text{charge}$$

As AgI/Ag^+ is a positive sol so negative ion will cause the coagulation.

Ions of the given electrolytes are, S^{2-}, PO_4^{3-}, SO_4^{2-} and Cl^-.

As Cl^- has minimum charge thus has maximum coagulating value.

21. (a): Many of the metals such as copper, silver, gold, aluminium, lead, etc. are purified by electrolytic refining.

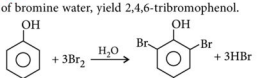
22. (c)

23. (a): V_2O_5 - amphoteric, Cr_2O_3 - amphoteric
Mn_2O_7 - acidic, CrO - basic
V_2O_4 - basic

24. (a)

25. (a): Alkyl halides are insoluble in water but soluble in organic solvent, polar in nature and undergo substitution or elimination reactions.

26. (a): Phenol forms a white precipitate with excess of bromine water, yield 2,4,6-tribromophenol.



2,4,6-tribromophenol (white ppt.)

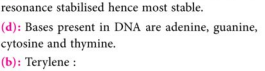
No such reaction takes place in alcohol.

27. (a): The compounds which have $CH_3-\overset{O}{\overset{\|}{C}}-$ or $CH_3-\underset{OH}{\underset{|}{CH}}-$ group can undergo haloform reactions. Thus, acetone (CH_3COCH_3) undergoes haloform reaction.

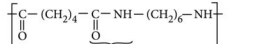
28. (b): Out of the given diazonium salts, $C_6H_5N_2^+X^-$ is resonance stabilised hence most stable.

29. (d): Bases present in DNA are adenine, guanine, cytosine and thymine.

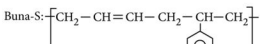
30. (b): Terylene :



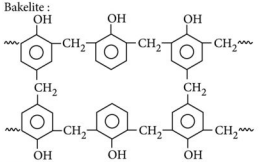
Nylon-6,6 :



Buna-S:



Bakelite :



31. (c)

32. (a): $\Lambda_m(\text{molar conductance}) = \dfrac{\kappa \times 1000}{M}$

$$\frac{\Lambda_m\,(\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1})}{\kappa\,(\text{ohm}^{-1}\,\text{cm}^{-1})} = \frac{1000}{M} = \frac{1000}{0.01}\,\text{cm}^3\,\text{mol}^{-1}$$
$$= 10^5\,\text{cm}^3\,\text{mol}^{-1}$$

33. (c): Two solutions having same osmotic pressure at same temperature are known as isotonic solutions to each other.

34. (d): Temperature coefficient 2 means rate of reaction doubles at every 10°C rise in temperature.

Thus, $\dfrac{k_{90°C}}{k_{30°C}} = 2^6 = 64$

35. (c)

36. (c): Aluminium is mainly isolated from bauxite ore which is generally contaminated with ferric oxide and silica.

37. (d): Pure nitrogen is obtained by heating sodium or barium azide in vacuum.

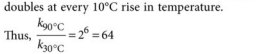
$$2NaN_3 \xrightarrow{\Delta} 3N_2 + 2Na$$

38. (b)

39. (b): Electronic configuration of X^{3+} : [Ar] $3d^5$
Electronic configuration of X will be : [Ar] $3d^6\,4s^2$
Thus, atomic number of transition element is 26.

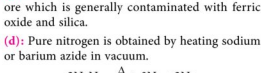
40. (a): $2CH_3{-}CH_2{-}CH_2{-}Cl + 2Na \xrightarrow{\text{Dry ether}} CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3 + 2NaCl$

41. (c):



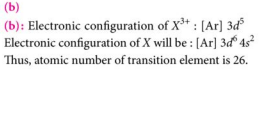
2-methyl propan-2-ol (test. alcohol) → 2-methylpropene

42. (c): Electron withdrawing groups increases the acidic strength of phenol while electron donating groups decreases the acidic strength.



(+*R*-effect) *p*-methoxyphenol (i) < (+*I*-effect) *p*-methylphenol (ii) < (−*R*, −*I*-effect) *p*-nitrophenol (iii)

43. (d):



Diphenylamine (Electrons delocalised in two rings)

(Electrons delocalised in three rings)

(Electrons are pulled by $-NO_2$ group due to $-I$ and $-R$-effect)

(No conjugation, so electrons will be easily available for donation)

(Conjugation in one ring)

44. (b)

45. (c): PVC and high density polythene are linear polymers. Low density polythene is branched chain polymer while bakelite is cross-linked polymer.

46. (c): Length of body diagonal
$= \sqrt{3} \times$ edge length of the cube (a)
$= \sqrt{3} \times 300$ pm $= 1.732 \times 300 = 519.6$ pm

47. (a)

48. (d): $\log_{10} K = \dfrac{-\Delta G^\circ}{2.303RT} = \dfrac{nFE^\circ_{cell}}{2.303RT}$ (at 25°C)

$$\log_{10} K = \frac{nE^\circ_{cell}}{0.0591} = \frac{2 \times 0.3}{0.0591} = 10 \quad \Rightarrow \quad K = 10^{10}$$

49. (a) **50. (a)**

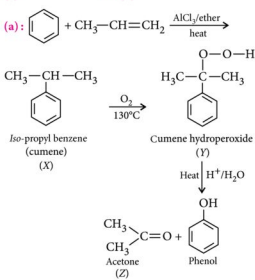
51. (b): $2PbO_2 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + O_2\uparrow$

52. (c): In alkaline medium:

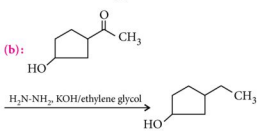
$2KMnO_4 + KI + H_2O \rightarrow 2KOH + 2MnO_2 + KIO_3$

53. (a) **54. (d)**

55. (a):

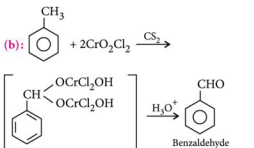


56. (b):

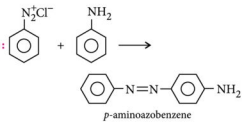


Both Zn-Hg/HCl and $NH_2NH_2OH^-$ can reduce $>C=O \longrightarrow >CH_2$ group but in case of Zn-Hg/HCl, HCl will bring about substitution of OH^- by Cl^-. therefore, the most effective reagent is NH_2NH_2, OH^-.

57. (b):

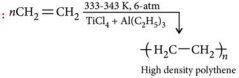


58. (b):



59. (d): In amylose α-*D* glucose units are linked to one another through α-glycosidic linkage involving C_1 of one glucose unit with C_4 of the other glucose unit.

60. (c):



$TiCl_4 + Al(C_2H_5)_3 \Rightarrow$ Ziegler-Natta catalyst.

For the SCIENTIST in YOU

Nitrogen-doped carbon catalyst improves efficiency of nitrogen reduction process

Ammonia is an essential fertiliser ingredient, with more than 145 million tonnes made around the world each year. It is produced by the Haber–Bosch process – a method developed over 100 years ago that now consumes between 3–5% of the world's natural gas. Ammonia production facilities are also enormously expensive, with upfront costs easily running into hundreds of millions of pounds.

A new electrochemical process could cut the carbon footprint and start-up costs of producing ammonia. The researchers working on the project hope that it could one day offer people in developing countries cheap, environmentally friendly fertilisers.

Transition metal catalyst helps produce sustainable hydrogen from urea

Scientists in China have developed a new catalyst, composed of highly porous nickel molybdenum oxide nanorods, that can catalyse the urea oxidation reaction more efficiently than any previously reported non-noble metal catalyst. This discovery could offer a more cost-effective and energy-efficient route for hydrogen production.

J&K CET

Jammu & Kashmir Common Entrance Test

SOLVED PAPER 2018

1. What product will form when *N*, *N*-dimethylaniline reacts with $NaNO_2$ and dilute HCl at low temperature?
(a) *p*-Nitroso-*N*, *N*-dimethylaniline
(b) Methyl-*n*-hexylamine
(c) *m*-Benzenediazonium chloride
(d) *N*-Nitroso-*N*-methylaniline

2. Of the following, which species is primarily obtained in a solution containing KHF_2?
(a) K^+, H^+ and F^- (b) H^+ and KF_2^-
(c) KF and H^- (d) K^+ and HF_2^-

3. What will be the equilibrium constant of the given reaction carried out in a 5 L vessel and having equilibrium amounts of A_2 and A as 0.5 mole and 2×10^{-6} mole respectively?
The reaction : $A_2 \rightleftharpoons 2A$
(a) 0.16×10^{-11} (b) 0.25×10^{5}
(c) 0.4×10^{-5} (d) 0.2×10^{-11}

4. How many electrons are involved during the oxidation reaction of $KMnO_4$ in acidic medium?
(a) 1 (b) 3 (c) 5 (d) 4

5. What will be the relation between the T_1 of gas 1 with $M_1 = 56$ and T_2 of gas 2 with $M_2 = 44$ if the average speed of gas 1 is equal to most probable speed of gas 2?
(a) $T_1 = T_2^2$ (b) $T_1 = T_2$
(c) $T_1 = (T_2)^{1/2}$ (d) $T_1 = 1/T_2$

6. What will be the correct unit of rate constant k for a reaction whose order is three?
(a) $mole^{-1}$ lit sec^{-1} (b) $mole^{2}$ lit sec^{-1}
(c) sec^{-1} (d) $mole^{-2}$ lit^{2} sec^{-1}

7. What is the hybridization and geometry of the compound $XeOF_4$?
(a) sp^3d^2 and octahedral
(b) sp^3d and square pyramidal
(c) sp^3d and trigonal bipyramidal
(d) sp^3d^2 and square pyramidal

8. Which of the following product(s) is/are formed when fructose is treated with Na-Hg in water?
(a) Sorbitol and Mannitol
(b) Sorbitol and *n*-Hexane
(c) Mannitol and *n*-Hexane
(d) Gluconic acid

9. What will be the correct decreasing order of acid strength of the hydroxybenzoic acids? (Symbols and notations carry their usual meanings)
(a) *p*-Hydroxybenzoic acid > benzoic acid > *m*-hydroxybenzoic acid > *o*-hydroxybenzoic acid
(b) *o*-Hydroxybenzoic acid > *m*-hydroxybenzoic acid > benzoic acid > *p*-hydroxybenzoic acid
(c) *o*-Hydroxybenzoic acid > benzoic acid > *m*-hydroxybenzoic acid > *p*-hydroxybenzoic acid
(d) *m*-Hydroxybenzoic acid > benzoic acid > *o*- hydroxybenzoic acid > *p*-hydroxybenzoic acid

10. What will be the products when benzaldehyde is treated with NaOD in D_2O?
(a) $C_6H_5CH_2OD$ and C_6H_5COONa
(b) $C_6H_5CH_2OD$ and C_6H_5COOD
(c) C_6H_5CHDOD and C_6H_5COONa
(d) $C_6H_5COOCHDC_6H_5$

11. Which of the following is the correct configuration of the complex $[RhCl_6]^{3-}$?
(a) High spin $t_{2g}^4e_g^2$ (b) Low spin $t_{2g}^6e_g^0$
(c) Low spin $t_{2g}^3e_g^3$ (d) High spin $t_{2g}^5e_g^1$

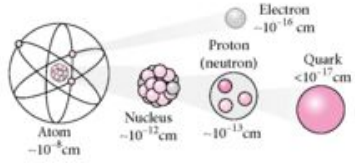
12. Dacron is continuous filament yarn used in curtains, dress fabrics and pressure fire hoses. The reaction for preparing dacron is by the combination of which of the following?
(a) Hexamethylene diamine and adipic acid
(b) Caprolactum
(c) Phenol and formaldehyde
(d) Ethylene glycol and terephthalic acid

CONCEPT MAP

STRUCTURE OF ATOM

Niels Henrik David Bohr (Niels Bohr), a Danish physicist who is generally regarded as one of the foremost physicists of the 20th century. He was the first to apply the quantum concept, to the problem of atomic and molecular structure. For that work he received the Nobel Prize in Physics in 1922. His manifold roles in the origins and development of quantum physics is his most important contribution.

FUNDAMENTAL PARTICLES



QUANTUM NUMBERS

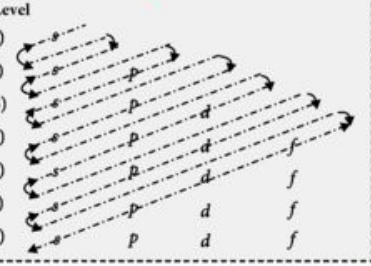
A set of four members which helps to determine the complete information about all the e^- in an atom.

Symbol	Quantum Numbers	Values	Role	
n	Principal	1, 2, 3,.....	Determines the energy (size).	
l	Angular	0, 1, 2, ... $n-1$	Special distribution of electron cloud and angular momentum.	
m_l	Magnetic	0, ±1, ±2, ... ±l	Determines the orientation in space.	
m_s	Spin	±1/2	Describes the electron spin (magnetic moment).	
l	0	1	2	3
Sub-shell	s	p	d	f
Orbital present	1	3	5	7

Rules for Assigning Electrons

- **Aufbau principle :** e^- occupy lowest energy orbital available.
- **Pauli exclusion principle :** Maximum 2 electrons per orbital must have opposite spins.
- **Hund's rule :** If two or more orbitals of equal energy are available, electrons will occupy them singly before filling in pairs.

Energy Level



ATOMIC MODELS

Thomson's Model (1904)

- Plum pudding model
- An atom was a sphere of positive electricity in which number of electrons were embedded, sufficient to neutralize the positive charge.

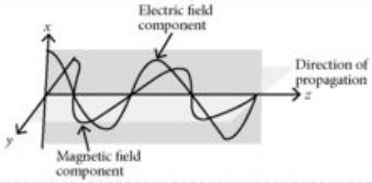
Rutherford's Model (1911)

The atom consists of two parts :

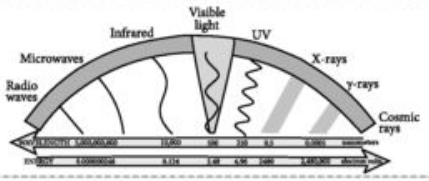
- **Nucleus :** Very small in size, carries positive charge.
- **Extra-nuclear part, *i.e.*, orbit :** Space around the nucleus in which electrons were distributed.

Electromagnetic Wave Theory

- James Maxwell (1870) suggested that when electrically charged particles move under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves, called electromagnetic waves or electromagnetic radiations.



- **Electromagnetic Spectrum :** The electromagnetic spectrum is a continuum of all electromagnetic waves arranged according to frequency and wavelength.
  Cosmic rays < γ-rays < X-rays < Ultra-violet rays < Visible < Infrared < Micro waves < Radio waves

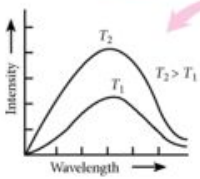


Particle Nature of Electromagnetic Radiations

- **Planck's Quantum Theory :** A body can emit or absorb energy only in terms of integral multiple of a quantum/photon.
  $E = nh\nu$;
  where, $n = 1, 2, 3,...$

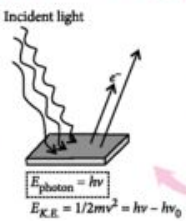
Black Body Radiation

If the substance being heated is a black body (which can emit and absorb all frequencies), the radiation emitted is called black body radiation.



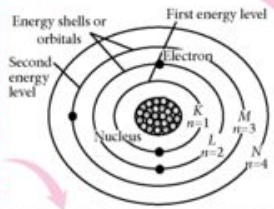
Photoelectric Effect

When radiations with frequency greater than a certain minimum frequency (ν_0) strike the surface of a metal, the electrons are ejected from the surface of the metal. This phenomenon is called photoelectric effect.



Bohr's Model

- An atom consist of a small heavy positively charged nucleus.
- The electrons revolve only in those orbits which have a fixed value of energy.



- **For hydrogen like atoms :**

$$E_n = \frac{-1312\,Z^2}{n^2}\ \text{kJ mol}^{-1} = -13.6\frac{Z^2}{n^2}\ \text{eV/atom}$$

Radius : $r_n = 52.9\dfrac{n^2}{Z}$ pm

Velocity of electrons : $v_n = 2.188 \times 10^8 \dfrac{Z}{n}\ \text{cm s}^{-1}$

Hydrogen Spectrum

According to Bohr's theory, an electron neither emits nor absorbs energy as long as it stays in a particular orbit.
However, an electron in an atom may jump from normal energy level, to some higher energy level. During each such jump, energy is emitted in the form of a photon ($h\nu$).

$E_2 - E_1 = h\nu = hc/\lambda$.

Different excited electrons adopts different routes to return to various lower energy levels.

Lyman series	:	From $n = 2, 3, 4$ ..... to $n = 1$
Balmer series	:	From $n = 3, 4, 5$ ..... to $n = 2$
Paschen series	:	From $n = 4, 5, 6$ ..... to $n = 3$
Brackett series	:	From $n = 5, 6, 7$ ..... to $n = 4$
Pfund series	:	From $n = 6, 7, 8$ ..... to $n = 5$

Towards Quantum Mechanical Model

- **Dual nature of matter :** Every material particle in motion has dual nature (particle and wave nature).

de-Broglie wavelength, $\lambda = \dfrac{h}{mv} = \dfrac{h}{P}$

- **Heisenberg's uncertainty principle :** It is impossible to measure simultaneously the exact position and momentum of an electron.

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

Quantum Mechanical Model

- The electrons in an atom have only quantized values of energy.
- These quantized values of energy are obtained from the solution of Schrodinger wave equation.

$$\frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dy^2} + \frac{d^2\Psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$$

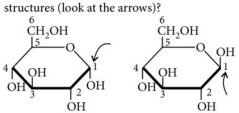
By finding Ψ^2 at different points around the nucleus in an atom, we can predict the region of space around the nucleus within which the probability of finding the electron is maximum.

13. What is the hybridization and geometry of the given species? The species are XeF_2 and ICl_2^-.
(a) sp^3d and trigonal bipyramidal
(b) sp^3d^2 and square planar
(c) sp^3d and linear
(d) sp^3 and irregular tetrahedron

14. What will be the heat change at constant volume for the reaction whose heat change at constant pressure is –560 kcal at 27 °C? The reaction is
$C_8H_{16} + 12O_2 \rightarrow 8CO_2 + 8H_2O$
(Given R = 2 cal $mol^{-1}K^{-1}$)
(a) –558200 calories (b) 442800 calories
(c) –561800 calories (d) 368240 calories

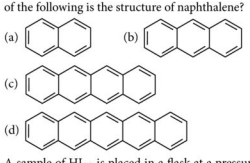
15. What will be the geometry of the compound MB_4L_2? Here B is bond pair and L is lone pair.
(a) Square planar (b) Octahedral
(c) Square pyramid (d) Tetrahedral

16. What is the relationship between the given structures (look at the arrows)?



α-*D*-glucopyranose β-*D*-glucopyranose
(a) Enantiomers (b) Anomers
(c) Diastereomers (d) Metamers

17. Naphthalene is a white, volatile, solid polycyclic hydrocarbon with a strong mothball odour. Which of the following is the structure of naphthalene?



18. A sample of $HI_{(g)}$ is placed in a flask at a pressure of 0.2 atm. At equilibrium, partial pressure of $HI_{(g)}$ is 0.04 atm. What is K_p for the given equilibrium?
$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$
(a) 0.04 (b) 0.4
(c) 40 (d) 4

19. The following equation is the Arrhenius equation, $k = Ae^{-E_a/RT}$, where E_a is the minimum energy molecules must possess in order to react to form a product, k is the rate constant, A is the frequency factor, R is the gas constant and T is the Kelvin temperature. Under normal circumstances, the Arrhenius plot is obtained by plotting
(a) logarithm of the inverse of rate constant 1/k, versus the inverse temperature 1/T
(b) logarithm of the rate constant k, versus the temperature T
(c) logarithm of the rate constant k, versus the inverse temperature 1/T
(d) logarithm of the inverse of rate constant 1/k, versus the temperature T.

20. What final product will form when alcoholic KOH is treated with 1, 1–dichloroethane?
(a) Ethane-1, 2-diol (b) Ethene
(c) Ethyne (d) Acetaldehyde

21. What will be the expression of K_p for the given reaction if the total pressure inside the vessel is P and degree of dissociation of the reactant is a? The reaction : $N_2O_4 \rightleftharpoons 2NO_2$
(a) $4a^2P/(1 + a^2)$ (b) $4a^2P/(1 - a^2)$
(c) $a^2P/(1 - a^2)$ (d) $a^2/(1 - a)$

22. What are the coordination numbers (C.N.) of Ca^{2+} and F^- ion in calcium fluoride (CaF_2) crystal structure?
(a) C.N. of Ca^{2+} = 4 and F^- = 8
(b) C.N. of Ca^{2+} = 6 and F^- = 6
(c) C.N. of Ca^{2+} = 8 and F^- = 8
(d) C.N. of Ca^{2+} = 8 and F^- = 4

23. What will be ionization energy of Be atom? Consider the first ionization energy of H atom as 13.6 eV.
(a) 27.2 eV (b) 54.4 eV
(c) 108.8 eV (d) 4 eV

24. What will be the half-cell potential of a hydrogen electrode acting as an anode and dipped in a solution of pH = 2?
(a) 0 V (b) 0.0196 V
(c) 0.276 V (d) 0.118 V

25. Which of the following is the correct reason for HI solution turning brown on exposure to air?
(a) HI reacts with H_2O to form I_2.
(b) HI dissolves NO_2.
(c) HI reacts with O_2 to form I_2.
(d) HI reacts with N_2 and O_2 to form NO_2.

26. Which of following compounds has a highly intense red colour at room temperature?
(a) $SnCl_4$ (b) SnI_4
(c) PbI_2 (d) $PbCl_2$

27. What will be the percentage of dimerization of 61 g of benzoic acid in 1000 g of a solvent and producing a depression in freezing point of 2 °C? Consider K_f to be 6.
(a) 72% (b) 67% (c) 43% (d) 28%

28. What is the IUPAC nomenclature of isoprene monomer present in natural rubber?
(a) 2-Methyl-1, 3-butadiene
(b) 1, 3-Hexadiene
(c) 2, 3-Dimethyl-1, 3-butadiene
(d) 2-Methyl-1, 3-pentadiene

29. Identify the correct increasing order of crystal field stabilization energy value for the given complexes.
(a) $[Ir(NH_3)_6]^{3+} < [Rh(NH_3)_6]^{3+} < [Co(NH_3)_6]^{3+}$
(b) $[Rh(NH_3)_6]^{3+} < [Co(NH_3)_6]^{3+} < [Ir(NH_3)_6]^{3+}$
(c) $[Co(NH_3)_6]^{3+} < [Ir(NH_3)_6]^{3+} < [Rh(NH_3)_6]^{3+}$
(d) $[Co(NH_3)_6]^{3+} < [Rh(NH_3)_6]^{3+} < [Ir(NH_3)_6]^{3+}$

30. What is the correct explanation of the non-reducing property of sucrose?
(a) α-*D*-glucopyranose and β-*D*-fructofuranose are linked *via* C_2 and C_1 centres respectively.
(b) α-*D*-glucopyranose and β-*D*-fructofuranose are linked *via* C_1 and C_2 centres respectively.
(c) α-*D*-glucopyranose and β-*D*-fructofuranose are linked *via* C_2 and C_2 centres respectively.
(d) α-*D*-glucopyranose and β-*D*-fructofuranose are linked *via* C_3 and C_4 centres respectively.

31. The number of times the comparative mass of a neutron is heavier than an electron is
(a) ~1842 (b) ~182
(c) ~102 (d) ~4050

32. With respect to atomic spectrum, each line in the Lyman series is due to electrons returning
(a) from a particular higher energy level to $n = 3$
(b) from a particular higher energy level to $n = 2$
(c) from a particular higher energy level to $n = 1$
(d) from a particular higher energy level to $n = 4$

33. In a reaction $A + B \rightleftharpoons C + D$, Le Chatelier's principle asserts that an equilibrium between *A* and *B* producing *C* and *D* can be shifted towards *C* and *D* by
(i) increasing the concentration of *A* or *B*
(ii) increasing the concentration of *C* or *D*
(iii) decreasing the concentration of *A* or *B*.
(a) (ii) only (b) Both (i) and (ii)
(c) (iii) only (d) (i) only

34. Identify the optically active cyclohexane from the given options.
(a) *trans*-1, 3-dimethyl cyclohexane
(b) *cis*-1, 3-dimethyl cyclohexane
(c) *cis*-1, 4-dimethyl cyclohexane
(d) *trans*-1, 4-dimethyl cyclohexane

35. What condition will facilitate the spontaneity of a reaction if ΔH and ΔS both are negative?
(a) Low temperature (b) High temperature
(c) Low pressure (d) High pressure

36. What will be the correct stability order of the different conformations of *n*-butane?
(a) Fully-eclipsed > eclipsed > gauche > anti-staggered
(b) Anti-staggered > eclipsed > gauche > fully-eclipsed
(c) Anti-staggered > gauche > eclipsed > fully-eclipsed
(d) Gauche > anti-staggered > eclipsed > fully-eclipsed

37. Identify the anti-aromatic system from among the given options.
(a) Benzene (b) [14]-Annulene
(c) [18]-Annulene (d) Cyclo-octatetraene

38. Which of the following shows the correct reaction for nitrobenzene reduction?
(a) Nitrobenzene reacts with Zn dust and NH_4Cl to produce aniline.
(b) Nitrobenzene reacts with $LiAlH_4$ to produce phenyl hydroxylamine.
(c) Nitrobenzene reacts with Fe and HCl to produce nitrosobenzene.
(d) Nitrobenzene reacts with Zn dust and NH_4Cl to produce phenyl hydroxylamine.

39. What will be the enthalpy of formation of NO_2 from the given bond dissociation enthalpy values? The bond dissociation enthalpy values for O_2, NO and NO_2 are as follows, $O_{2(g)}$: 0 kJ/mol, $NO_{(g)}$: 90.25 kJ/mol and $NO_{2(g)}$: 33.18 kJ/mol respectively.
(a) +114.1 kJ (b) +52.7 kJ
(c) −52.7 kJ (d) −114.1 kJ

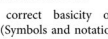
40. What will be the resultant product when ethoxybenzene is reacted with HI?
(a) Phenyl iodide and ethanol
(b) Ethyl benzene
(c) Phenol and ethyl iodide
(d) *p*-Ethyl phenol

41. What will be the nature of existence of an amino acid (containing one amino and one carboxylic acid group) in solution of pH < pK_{a_1}?
(a) It exists as anion.
(b) It exists as cation.
(c) It exists as zwitter ion.
(d) It exists as neutral species with no charge.

42. What will be the geometry and magnetic moment of the complex $[NiCl_4]^{2-}$?
(a) Tetrahedral and 3.87 B.M.
(b) Tetrahedral and 2.82 B.M.
(c) Square planar and 2.82 B.M.
(d) Square planar and 4.89 B.M.

43. Identify the correct basicity order in the nitroanilines? (Symbols and notations carry their usual meaning.)
(a) *o*-Nitroanilines < *p*-nitroanilines < *m*-nitroanilinies
(b) *m*-Nitroanilines < *p*-nitroanilines < *o*-nitroanilinies
(c) *p*-Nitroanilines < *o*-nitroanilines < *m*-nitroanilinies
(d) *o*-Nitroanilines < *m*-nitroanilines < *p*-nitroanilines

44. What is the IUPAC nomenclature of the given compound?



(a) 5-Ethynyl-1, 6-heptadiene
(b) 3-Ethynyl-1, 6-heptadiene
(c) 3-Vinyl-hept-6-en-1-yne
(d) 5-Vinyl-hept-1-en-6-yne

45. Which electronic configuration will show the highest first ionization potential?
(a) $1s^2 2s^2 2p^1$ (b) $1s^2 2s^2 2p^5$
(c) $1s^2 2s^2 2p^3$ (d) $1s^2 2s^2$

46. Which of the statements is true regarding chemisorption of a gas on a solid surface?
(a) This type adsorption first increases with increase of temperature.
(b) No compound formation takes place in this case.
(c) The forces operating in this are weak van der Waals' forces.
(d) It forms multimolecular layers of gas molecules on the surface.

47. What will be the entropy change of the system when expansion of 1 mole of a gas takes place from 3 L to 6 L under isothermal conditions? Consider, $R = 2$ cal $K^{-1}mol^{-1}$ and $\log 2 = 0.301$.
(a) 2.84 cal K^{-1} (b) 1.386 cal K^{-1}
(c) 0.37 cal K^{-1} (d) 5.26 cal K^{-1}

48. What is the main product formed when iodine reacts with hypo?
(a) Na_2SO_4 (b) $Na_2S_4O_6$
(c) Na_2SO_3 (d) Na_2S

49. What will be the resultant products formed when the phosphorus halide PBr_5 splits up?
(a) $[PBr_4]^+$ and Br^- (b) $[PBr_6]^-$ and $[PBr_4]^+$
(c) $[PBr_4]^+$ (d) $[PBr_6]^-$

50. What is the correct increasing order of ionic or atomic radii in the following?
(a) $Si^{4+} < P^{5+} < S^{6+} < Cl^{7+}$
(b) $P^{5+} < Si^{4+} < Cl^{7+} < S^{6+}$
(c) $Cl^{7+} < S^{6+} < P^{5+} < Si^{4+}$
(d) $S^{6+} < P^{5+} < Cl^{7+} < Si^{4+}$

51. Which equation will explain the nature of *PV* versus *P* curve for CO_2 gas at moderately low pressure?
(a) $PV = RT + Pb$ (b) $PV = RT + a/V$
(c) $PV = RT - a/V$ (d) $PV = RT - aV$

52. Which of the following statements is/are true for an electrochemical cell?
(a) Oxidation occurs at the anode only.
(b) Reduction occurs at the anode only.
(c) Oxidation occurs at both the anode and cathode.
(d) Reduction occurs at both the anode and cathode.

53. How many geometrical isomers are possible with complexes of the type $[M(ab)_3]$?
(a) 2 (b) 4
(c) 3 (d) 5

54. What is the number of octahedral void(s) per atom present in a cubic close-packed structure?
(a) 1 (b) 3
(c) 2 (d) 6

55. What product is formed when phenol is treated with $CHCl_3$ and NaOH?

(a) 3-Hydroxybenzaldehyde
(b) 2-Hydroxybenzoic acid
(c) 3-Hydroxybenzoic acid
(d) 2-Hydroxybenzaldehyde

56. Which of the following is a branched polymer, having branched chain polysaccharide units?
(a) Starch
(b) Bakelite
(c) High density polyethylene
(d) Nylon

57. Which of the following is the correct increasing order of coagulating power of electrolytes required to precipitate a negatively charged As_2S_3 colloid?
(a) $NaCl < BaCl_2 < AlCl_3$
(b) $BaCl_2 < AlCl_3 < NaCl$
(c) $AlCl_3 < NaCl < BaCl_2$
(d) $AlCl_3 < BaCl_2 < NaCl$

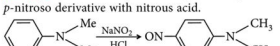
58. Calculate the molarity of a solution of 30 g of $Co(NO_3)_2.6H_2O$ in 4.3 L of solution? Consider atomic mass of Co = 59u, N = 14u, O = 16u, H = 1u
(a) 0.023 M (b) 0.23 M
(c) 0.046 M (d) 0.46 M

59. What will be the E_{cell} for the given cell?
$Zn|Zn^{2+}(0.1\ M)||Cu^{2+}(0.01\ M)|Cu$
Given : $E^{\circ}_{Zn^{2+}/Zn} = 0.76$ V and $E^{\circ}_{Cu^{2+}/Cu} = 0.34$ V.
Also predict whether the reaction is spontaneous or non-spontaneous.
(a) 1.07 V and spontaneous
(b) −1.13 V and non-spontaneous
(c) −1.07 V and non-spontaneous
(d) 1.13 V and spontaneous

60. Which of the manganese oxides is the most acidic from the given options?
(a) Mn_2O_3 (b) MnO
(c) MnO_2 (d) Mn_2O_7

SOLUTIONS

1. (a) : *N*,*N*-Dimethylaniline (3°amine) forms *p*-nitroso derivative with nitrous acid.



p-nitroso-*N*, *N*-dimethylaniline

2. (d) : $KHF_2 \rightleftharpoons K^+ + HF_2^-$

3. (a) : $A_2 \rightleftharpoons 2A$

Concentration of A_2 at equilibrium = $\frac{0.5}{5}$

Concentration of A at equilibrium = $\frac{2\times10^{-6}}{5}$

Equilibrium constant, $K_c = \frac{[A]^2}{[A_2]} = \frac{\left(\frac{2\times10^{-6}}{5}\right)^2}{\frac{0.5}{5}}$

$= \frac{4\times5}{25\times0.5}\times10^{-12} = 0.16\times10^{-11}$

4. (c) : Reaction of $KMnO_4$ in acidic medium :
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

5. (b) : $c_{av} = \sqrt{\frac{8RT}{\pi M}}$; $c_{mp} = \sqrt{\frac{2RT}{M}}$

Given that, $\sqrt{\frac{8RT_1}{\pi M_1}} = \sqrt{\frac{2RT_2}{M_2}} \Rightarrow \frac{8T_1}{\pi M_1} = \frac{2T_2}{M_2}$

$\frac{4T_1}{\pi\times56} = \frac{T_2}{44} \Rightarrow \frac{T_1}{T_2} = \frac{56\times\pi}{44\times4} = 1 \Rightarrow T_1 = T_2$

6. (d) : For third order reaction : Rate = $k[A]^3$
Mol L^{-1} sec^{-1} = k[Mol $L^{-1}]^3$

$k = \frac{\text{Mol L}^{-1}\text{ sec}^{-1}}{\text{Mol}^3\text{ L}^{-3}} = \text{Mol}^{-2}\text{ L}^2\text{ sec}^{-1}$

7. (d) : Number of hybrid orbitals

$= \frac{1}{2}$(V.E. + M.A. − c + a)

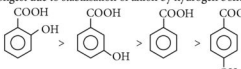
For, $XeOF_4$
V.E. = 8 ; M.A. (monovalent atoms) = 4

$= \frac{1}{2}(8+4) \Rightarrow 6$ *i.e.*, sp^3d^2 hybridisation

Square pyramidal

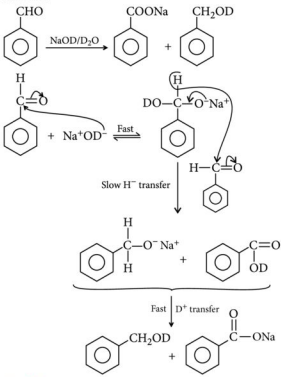
8. (a) :

9. (b) : In case of hydroxybenzoic acids, they display both kind of effect and there is a decrease in electron density at all positions due to inductive effect of –OH group, but increase in electron density at *o*- and *p*-positions due to resonance effect by –OH group. So, *o*- *p*-hydroxybenzoic acids should be weaker than *m*-hydroxybenzoic acid, but *o*-hydroxybenzoic acid is strongest due to stabilisation of anion by hydrogen bonding.



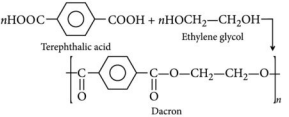
o-hydroxy benzoic acid ($pK_a = 2.98$) | *m*-hydroxy benzoic acid ($pK_a = 4.08$) | Benzoic acid ($pK_a = 4.19$) | *p*-hydroxy benzoic acid ($pK_a = 4.58$)

10. (a) : Benzaldehyde on treatment with 50% aqueous or ethanolic alkali solution undergoes Cannizzaro reaction *i.e.*, one molecule is oxidised and one is reduced.



11. (b) : Elements of 4*d* and 5*d* series are more prone to spin pairing therefore they form low spin complexes.

12. (d) : Terylene or dacron is a polyester, which is prepared by condensing terephthalic acid and ethylene glycol.

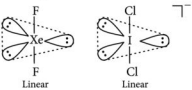


13. (c) : Number of hybrid orbitals (X)

$$= \frac{1}{2}[\text{V.E.} + \text{M.A.} - c + a]$$

For XeF_2 : $(X) = \frac{1}{2}(8+2) = 5$ *i.e.*, sp^3d hybridisation

For ICl_2^- : $(X) = \frac{1}{2}(7+2+1) = 5$ *i.e.*, sp^3d hybridisation



14. (None) :

$\Delta H = -560$ kcal $\qquad \Delta E = ?$

$C_8H_{16(l)} + 12O_{2(g)} \longrightarrow 8CO_{2(g)} + 8H_2O_{(l)}$

$\Delta H = \Delta E + \Delta n_g RT$

$\Delta E = \Delta H - \Delta n_g RT$

$= -560{,}000 - (-4 \times 2 \times 300) = -560{,}000 + 2400$

$= -5{,}57{,}600$ cal

15. (a) : The structure of the compound will be octahedral with two lone pairs.

So, geometry is square planar.

16. (b) : The isomers which differ in position at C-1 carbon are known as anomers.

17. (a)

18. (d) :

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

At $t = 0$	0.2	0	0
At equilibrium	$(0.2 - 2x)$	x	x

$0.2 - 2x = 0.04 \Rightarrow 2x = 0.2 - 0.04$

$x = 0.08$ atm

$$K_p = \frac{(0.08)(0.08)}{(0.04)^2} = 4$$

19. (c) : $k = Ae^{-E_a/RT}$

Taking log on both sides

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

Logarithm of k is plotted against $(1/T)$ to obtain Arrhenius plot.

20. (c) : $CH_3-CH(Cl)_2 \xrightarrow[-HCl]{KOH} CH_2=CH-Cl$ (1,1-Dichloroethane → Vinyl chloride)

$\xrightarrow[-HCl]{KOH} CH\equiv CH$ (Ethyne)

21. (b) :

	$N_2O_4 \rightleftharpoons$	$2NO_2$
Moles at $t = 0$	1	0
Moles at equilibrium	$1 - a$	$2a$

Total moles at equilibrium $= 1 - a + 2a = 1 + a$

$$P_{N_2O_4} = \left(\frac{1-a}{1+a}\right)P; \quad P_{NO_2} = \left(\frac{2a}{1+a}\right)P$$

$$K_p = \frac{P_{NO_2}}{P_{N_2O_4}} = \frac{\left(\frac{2a}{1+a}\right)^2 P^2}{\left(\frac{1-a}{1+a}\right)P} = \frac{4a^2P}{1-a^2}$$

22. (d) : Each Ca^{2+} ion is surrounded by 8 F^- ions and each F^- ion by 4 Ca^{2+} ions. Thus, coordination number of Ca^{2+} is 8 and F^- is 4.

23. (None) : Ionisation energy = –(energy of first orbit)

Energy of the 1st orbit of hydrogen = –13.6 eV

Energy of the 1st orbit of $Be^{3+} = Z^2 \times -13.6$

$= (4)^2 \times -13.6$

Ionisation of 1st orbit by $Be^{3+} = -(-13.6 \times 16) = 217.6$ eV

Note : Consider Be^{3+} ion (1 electron system) instead of Be atom in the question.

24. (None) : $E = -\frac{2.303RT}{F}\text{pH} = -0.059 \times 2 = -0.118$

25. (c) : HI is strong reducing agent. Its aqueous solution get oxidised even by atmospheric oxygen.

$$4HI + O_2 \longrightarrow 2H_2O + 2I_2$$

26. (b) : $SnCl_4$ — Colourless or slightly yellow

SnI_4 — Red - orange solid

PbI_2 — Yellow solid

$PbCl_2$ — White solid

27. (b) : $w_{\text{benzoic acid}} = 61$ g; $W_{\text{solvent}} = 1000$ g

$\Delta T_f = 2°C$; $K_f = 6$

$\Delta T_f = iK_f m$

$$m = \frac{61/122}{1000} \times 1000 = 0.5; \; i = \frac{\Delta T_f}{k_f m} = \frac{2}{6 \times 0.5} = 0.67$$

$$\alpha = \frac{1-i}{1-1/n} \qquad n = 2 \text{ for benzoic acid}$$

$$\alpha = \frac{1-0.67}{1-0.5} = 0.66 = 66\%$$

28. (a) : $CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2$

(Isoprene or 2-methylbut-1,3-diene)

29. (d) : The elements in the 2nd and 3rd transition series (the 4*d* and 5*d* elements) have large splitting than those in 3*d* series. So, the order of CFSE is

$[Co(NH_3)_6]^{3+} < [Rh(NH_3)_6]^{3+} < [Ir(NH_3)_6]^{3+}$

30. (b) : Sucrose is a non-reducing sugar since, both glucose ($C_1 - \alpha$) and fructose ($C_2 - \beta$) are connected to each other through their reducing centres.

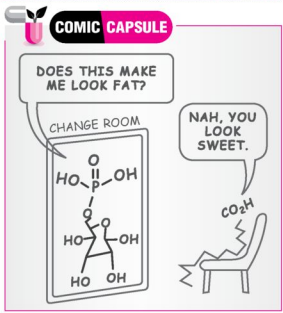
31. (a)

32. (c) : Lyman series : From $n = 2, 3, 4, 5....$ to $n = 1$.

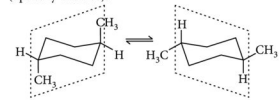
33. (d) : According to Le-Chatelier's principle "If a system in equilibrium is subjected to a change in any of the factors that determine the equilibrium conditions of a system then the equilibrium will shift in the direction so, as to reduce or to counteract the effect of the change.

$$A + B \rightleftharpoons C + D$$

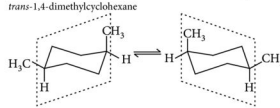
Thus, in the given equilibria, if concentration of *A* and *B* is increased the reaction will move in forward direction to reduce the effect of increase in concentration of *A* and *B*.



34. (a) : *cis*- and *trans*-1,4-dimethylcyclohexane contain an internal symmetry plane, only two stereoisomers appear. Therefore, they are both meso compounds (optically inactive).

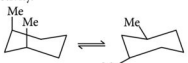


trans-1,4-dimethylcyclohexane

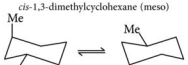


cis-1,4-dimethylcyclohexane

In contrast to 1,4-dimethylcyclohexane, only *cis*-1,3-dimethylcyclohexane contains an internal symmetry plane, while *trans*-1,3-dimethylcyclohexane does not. Thus, *cis*-1,3-dimethylcyclohexane is a *meso* compound, and *trans*-1,3-dimethylcyclohexane shows optical activity.



cis-1,3-dimethylcyclohexane (meso)



trans-(1*S*,3*S*)-1,3-dimethylcyclohexane

35. (a) : For a reaction to be spontaneous, ΔG of the reaction should be negative.

$\Delta G = \Delta H - T\Delta S$

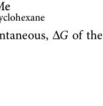
Given that $\Delta H = -ve$, $\Delta S = -ve$

$\Delta G = -\Delta H + T\Delta S$

So, at low value of temperature only, ΔG will be negative.

36. (c) :

(I)
Total or fully eclipsed



(II)
Gauche or skew

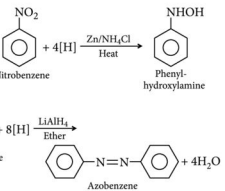
(III)
Eclipsed

(IV)
Anti (staggered)

The overall stability order is : (IV) > (II) > (III) > (I) *i.e* Anti (staggered) > Guache (Skew) > Eclipsed > Fully eclipsed

37. (None) : Benzene, [14]annulene and [18]annulene are aromatic. Benzene is fully planar, though [14] and [18]annulene with all *trans* double bonds (placing the hydrogens inside the ring) can achieve the planar conformation needed for aromaticity, with [14] and [18] annulene following Hückel's rule ($4n+2\ \pi$ electrons). Cyclooctatetraene (C_8H_8) has $8\ \pi$ electrons, so it is a misconception that it is anti-aromatic ($4n$ system, $n = 2$). However, actually the molecule takes a tub-shaped conformation in its native state. Since, it is not a planar molecule, it becomes non-aromatic instead of anti-aromatic.

38. (d) :



39. (d) : $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

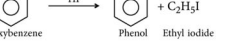
$\Delta H°_{reaction} = \Sigma\Delta H_{f(products)} - \Delta H_{f(reactants)}$

$= (2 \times 33.18) - (2 \times 90.25 + 0)$

$\Delta H°_{reaction} = -114.1$ kJ

Note : The values given are enthalpy of formation ($\Delta H°_f$).

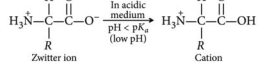
40. (c) :



41. (b) : At low pH (acidic solution) COO^- ion acts as the base and accepts a proton to form the cation.

42. (b) : $Ni^{2+} \Rightarrow [Ar]\ 3d^8$

In weak field ligand, pairing does not take place.

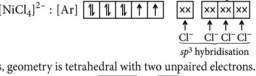


So, $[NiCl_4]^{2-}$: [Ar]

Thus, geometry is tetrahedral with two unpaired electrons.

Magnetic moment = $\sqrt{n(n+2)} = \sqrt{2(4)} = 2.82$ B.M.

43. (a) : Increasing basicity order of nitroanilines :



ortho substituted anilines are weaker bases than others probably due to a combination of steric and electronic factors. This is called *ortho* effect.

44. (b) :

3-Ethynyl-1,6-heptadiene

45. (b) : $1s^2 2s^2 2p^1 \Rightarrow$ B

$1s^2 2s^2 2p^5 \Rightarrow$ F

$1s^2 2s^2 2p^3 \Rightarrow$ N

$1s^2 2s^2 \Rightarrow$ Be

The order of first ionisation enthalpies is F > N > Be > B.

46. (a) : Chemisorption involves strong valence bond forces and monolayered. It first increase with increase in temperature and then decreases after a certain temperature.

47. (b) : $n = 1,\ V_i = 3$ L, $V_f = 6$ L

$$\Delta S = 2.303\ nR \log_{10} \frac{V_f}{V_i}$$

$$\Delta S = 2.303 \times 1 \times 2 \log \frac{6}{3} = 2.303 \times 2 \times 0.3010 = 1.386 \text{ cal K}^{-1}$$

48. (b) : $2Na_2S_2O_3 + I_2 \longrightarrow \underset{\text{Hypo}}{Na_2S_4O_6} + 2NaI$

49. (a) : $PBr_5 \rightleftharpoons [PBr_4]^+ [Br^-]$

PBr_5 splits into stable tetrahedral structure as $[PBr_4]^+$ and $[Br^-]$.

50. (c) : For isoelectronic species, higher the positive charge lower will be the ionic radius.

51. (c) : van der Waals' equation is

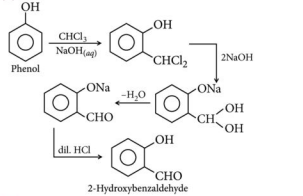
$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

At low pressures, the volume is sufficiently large and therefore b can be neglected in comparison to V.

$$\left(P + \frac{a}{V^2}\right)(V) = RT \text{ or } PV = RT - a/V$$

52. (a) **53. (a)** **54. (a)**

55. (d) :



56. (a)

57. (a) : Coagulating power of an electrolyte is directly proportional to the fourth power of the valency of the oppositely charged ion of the electrolyte being added. The order will be $Na^+ < Ba^{2+} < A1^{3+}$.

58. (a) : Mass = 30 g

Molar mass = 59 + 14 × 2 + 12 × 16 + 12 × 1 = 291

$$\text{Moles of } Co(NO_3)_2 \cdot 6H_2O = \frac{30}{291}$$

$$\text{Molarity} = \frac{30}{291 \times 4.3} = 0.023 \text{ M}$$

59. (a) : $Zn|Zn^{2+}(0.1\text{ M})||Cu^{2+}(0.01\text{M})|Cu$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E^\circ_{cell} = E^\circ_{(Cu^{2+}/Cu)} - E^\circ_{(Zn^{2+}/Zn)}$$
$$= 0.34 - (-0.76) = 1.10 \text{ V}$$

$$E_{cell} = 1.10 - \frac{0.0591}{2} \log \frac{0.1}{0.01}$$

$E_{cell} = 1.10 - 0.03 = 1.07$

As E_{cell} is positive, the reaction is spontaneous.

60. (d)

SOLVED PAPER **2018**

Kerala PET

1. Which element has the highest first ionization potential?
(a) N (b) Ne (c) He (d) H
(e) Li

2. Which statements(s) is (are) false for the periodic classification of elements?
(a) The properties of the elements are the periodic functions of their atomic numbers.
(b) Non-metallic elements are lesser in number than the metallic elements.
(c) The first ionization energies of the elements along a period do not vary in a regular manner with increase in atomic number.
(d) For transition elements, the *d*-electrons are filled monotonically with increase in atomic number.
(e) Both (c) and (d).

3. The electronegativities of N, C, Si and P are in the order
(a) P < Si < C < N (b) Si < P < N < C
(c) Si < P < C < N (d) P < Si < N < C
(e) difficult to predict.

4. Gd(64) has _____ unpaired electrons with sum of spin _____
(a) 7, 3.5 (b) 8, 3 (c) 6, 3 (d) 8, 4
(e) 9, 3.5

5. When SO_2 gas is passed into aqueous Na_2CO_3, the product(s) formed is (are)
(a) $NaHSO_4$ (b) Na_2SO_4
(c) $NaHSO_3$ (d) Na_2SO_3 and $NaHSO_3$
(e) $NaHSO_4$ and Na_2SO_4

6. Portland cement does not contain
(a) $CaSiO_4$ (b) $CaSiO_3$
(c) $Ca_3Al_2O_6$ (d) $Ca_3(PO_4)_2$
(e) Both (c) and (d).

7. $Al_2(SO_4)_3$ is used in the following but not
(a) as a coagulant in treating drinking water and sewage
(b) in plastic industry (c) as a mordant in dyeing
(d) in paper industry (e) both (c) and (d).

8. Maximum number of covalent bonds formed by N and P are
(a) 3, 5 (b) 3, 6
(c) 3, 4, 5 (d) 3, 4, 6
(e) none of the above.

9. Consider the following statements concerning N_2H_4.
1. It is an exothermic compound.
2. It burns in air with the evolution of heat.
3. It has kinetic stability.
4. It reduces Fe^{3+} to Fe^{2+} in acidic medium.
Which of the following combination is correct?
(a) 2 and 3 are correct (b) 1 and 2 are correct
(c) All are correct (d) 3 and 4 are correct
(e) 2, 3 and 4 are corect

10. Consider the following species,
1. $[O_2]^{2-}$ 2. $[CO]^+$ 3. $[O_2]^+$
Among these, sigma bond alone is present in
(a) 1 alone (b) 2 alone
(c) 3 alone (d) 1 and 2
(e) 1, 2 and 3

11. Select the correct option(s) for the following statements.
1. Cl_2O and ClO_2 are used as bleaching agents.
2. OCl^- salts are used as detergents.
3. OCl^- disproportionates in alkaline medium.
4. BrO_3^- is oxidized in acidic medium.
(a) 1, 2, 3 correct (b) 2, 3, 4 correct
(c) 1, 2, 4 correct (d) 1, 3, 4 correct
(e) All are correct

12. When H_2O_2 is added to an acidified $K_2Cr_2O_7$ solution
(a) a green colour solution is obtained
(b) a yellow solution is obtained
(c) a blue-violet solution is obtained
(d) a green precipitate is formed
(e) a yellow precipitate is formed.

13. Consider the following compounds
(1) $(NH_4)_2Cr_2O_7$ (2) NH_4NO_2
(3) NH_4VO_3 (4) NH_4NO_3
Which compounds(s) yield nitrogen gas upon heating?
(a) 1 and 2 (b) 2 and 3
(c) 3 and 4 (d) 1 and 4
(e) All

14. How many peroxy linkages are present in CrO_5?
(a) 1 (b) 2 (c) 3 (d) 4
(e) 5

15. More than four bonds are made by how many elements in carbon family?
(a) 1 (b) 2 (c) 3 (d) 4
(e) 5

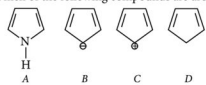
16. The effective nuclear charge of an element with three valence electrons is 2.60. What is the atomic number of the element?
(a) 1 (b) 2 (c) 3 (d) 4
(e) 5

17. The elution sequence of a mixture of compounds containing chlorobenzene, anthracene and *p*-cresol developed on an alumina column using a solvent system of progressively increasing polarity is
(a) anthracene → chlorobenzene → *p*-cresol
(b) anthracene → *p*-cresol → chlorobenzene
(c) chlorobenzene → *p*-cresol → anthracene
(d) chlorobenzene → anthracene → *p*-cresol
(e) *p*-cresol → anthracene → chlorobenzene.

18. Number of constitutional isomers of alkane with formula C_6H_{14} is
(a) 3 (b) 2 (c) 5 (d) 10
(e) 8

19. Phenylacetylene on treatment with $HgSO_4/H_2SO_4$, H_2O produces
(a) acetophenone (b) phenylacetaldehyde
(c) phenylacetic acid (d) 1-phenylethanol
(e) 2-phenylethanol.

20. Which of the following compounds are aromatic?



A *B* *C* *D*

(a) *A*, *B* (b) *A*, *B*, *C*
(c) *B*, *C* (d) *B*, *C*, *D*
(e) *A*, *B*, *D*

21. Aromatic electrophilic substitution reaction that is reversible is
(a) nitration (b) chlorination
(c) sulphonation (d) alkylation
(e) acylation.

22. Which one of the following statements is false?
(a) *R* and *S* configurations correspond to the enantiomers of an optically active compound.
(b) The process of converting an optically active compound into a racemate is called racemization.
(c) A molecule containing a plane of symmetry can be optically active.
(d) Optical isomers that are not enantiomers are called diastereoisomers.
(e) All chiral objects are asymmetric.

23. Neopentyl bromide undergoes dehydro-halogenation to give alkenes even though it has no β-hydrogen. This is due to
(a) *E*2 mechanism
(b) *E*l mechanism
(c) rearrangement of carbocations by *E*l mechanism
(d) *E*1*CB* mechanism
(e) *E*1 mechanism.

24. The compound which does not lead to nitrile by substitution with NaCN/DMSO is
(a) benzyl chloride (b) ethyl chloride
(c) *iso*-propyl chloride (d) chlorobenzene
(e) *iso*-butyl chloride.

25. Oxidation of 1° alcohols to aldehydes is very successful for the alcohols like
(a) pent-2-yn-1-ol (b) 1-hexanol
(c) *n*-propylalcohol (d) 1-pentanol
(e) 1-octanol.

26. The compound that does not undergo haloform reaction is
(a) acetaldehyde (b) ethanol
(c) acetone (d) acetophenone
(e) propiophenone.

27. The halogen compound which will not react with phenol to give ethers is
(a) ethyl chloride (b) methyl chloride
(c) benzyl chloride (d) vinyl chloride
(e) allyl chloride.

28. The weakest among the following acids is
(a) peroxyacetic acid (b) acetic acid
(c) chloroacetic acid (d) trichloroacetic acid
(e) propanoic acid.

29. The nitrosation of *N*,*N*-dimethylaniline takes place through the attack of electrophile
(a) nitronium ion (b) protonated nitrous acid
(c) nitrous acid (d) nitrite ion
(e) nitrosonium ion.

30. The nitrogenous base present only in RNA is
(a) guanine (b) adenine
(c) cytosine (d) uracil
(e) thymine.

31. Green fuel is the fuel obtained from
(a) bio-waste (b) metal waste
(c) plastic waste (d) chemical waste
(e) electronic waste.

32. Barbiturates are potent
(a) hypnotics (b) antimicrobials
(c) antacids (d) antiseptics
(e) antiallergics.

33. 1 mole of $FeSO_4$ (atomic weight of Fe is 55.84 g mol^{-1}) is oxidized to $Fe_2(SO_4)_3$. Calculate the equivalent weight of ferrous ion
(a) 55.84 (b) 27.92
(c) 18.61 (d) 111.68
(e) 83.76

34. Mass % of carbon in ethanol is
(a) 52 (b) 13 (c) 34 (d) 90
(e) 80

35. One mole of ethanol is produced reacting graphite, H_2 and O_2 together. The standard enthalpy of formation is –277.7 kJ mol^{-1}. Calculate the standard enthalpy of the reaction when 4 moles of graphite is involved.
(a) –277.7 (b) –555.4
(c) –138.85 (d) –69.42
(e) –1110.8

36. Which of the following process best describes atomization of $CH_{4(g)}$?
(a) Exothermic (b) Endothermic
(c) Non-spontaneous (d) Spontaneous
(e) Both (b) and (c)

37. Consider the equilibrium, $X_2 + Y_2 \rightleftharpoons ? P$. Find the stoichiometric coefficient of the *P* using the data given in the following table.

X_2/mol L^{-1}	Y_2/mol L^{-1}	P/mol L^{-1}
1.14×10^{-2}	0.12×10^{-2}	2.52×10^{-2}
0.92×10^{-2}	0.22×10^{-2}	3.08×10^{-2}

(a) 1 (b) 2 (c) 3 (d) 0.5
(e) 4

38. Which of the following can help predict the rate of a reaction if the standard Gibbs' free energy of reaction ($\Delta_r G°$) is known?
(a) Equilibrium constant
(b) $\Delta_r H°$ (c) $\Delta_r U°$
(d) Heat liberated during the course of reaction in calorimeter.
(e) both (b) and (a)

39. If 1 mole of NaCl solute is dissolved into the 1 kg of water, at what temperature will water boil at 1.013 bar? (K_b of water is 0.52 K kg mol^{-1}).
(a) 373.15 K (b) 373.67 K
(c) 374.19 K (d) 373.19 K
(e) 375 K

40. Calculate the molarity of a solution containing 5 g of NaOH dissolved in the product of a $H_2 - O_2$ fuel cell operated at 1 A current for 595.1 hours. (Assume 1F = 96500 C/mol of electrons and molecular weight of NaOH as 40 g mol^{-1})
(a) 0.05 M (b) 0.025 M
(c) 0.1 M (d) 0.075 M
(e) 1 M

41. Consider the electrochemical reaction between $Ag_{(s)}$ and $Cl_{2(g)}$ electrodes in 1 litre of 0.1 M KCl aqueous solution. Solubility product of AgCl is 1.8×10^{-10} and $F = 96500$ C/mol. At 1 μA current, calculate the time required to start observing the AgCl precipitation in the galvanic cell.
(a) 173 s (b) 346 s
(c) 1.25×10^6 s (d) 1.25×10^5 s
(e) 101 s

42. The voltage of the cell consisting of $Li_{(s)}$ and $F_{2(g)}$ electrodes is 5.92 V at standard condition at 298 K. What is the voltage if the electrolyte consists of 2 M LiF. ($\ln 2 = 0.693$, $R = 8.314$ J K^{-1} mol^{-1} and F = 96500 C mol^{-1})

(a) 5.90 V (b) 5.937 V
(c) 5.88 V (d) 4.9 V
(e) 4.8 V

43. Consider the galvanic cell,
$Pt(s)|H_2$ (1 bar)| HCl(aq) (1 M)| Cl (1 bar)|$Pt(s)$.
After running the cell for sometime, the concentration of the electrolyte is automatically raised to 3 M HCl. Molar conductivity of the 3 M HCl is about 240 S cm^2 mol^{-1} and limiting molar conductivity of HCl is about 420 S cm^2 mol^{-1}. If K_b of water is 0.52 K kg mol^{-1}, calculate the boiling point of the electrolyte at the end of the experiment.
(a) 375.6 K (b) 376.3 K
(c) 378.1 K (d) 380.3 K
(e) 381.6 K

44. The data given below are for the reaction of A and D_2 to form product at 295 K. Find the correct rate expression for this reaction.

D_2 / mol L^{-1}	A/mol L^{-1}	Initial rate/ mol L^{-1} s^{-1}
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) $k[D_2]^1\,[A]^2$ (b) $k[D_2]^2\,[A]^1$
(c) $k[D_2]^1\,[A]^1$ (d) $k[D_2]^2\,[A]^2$
(e) $k[D_2]^1\,[A]^0$

45. Find the unit of the rate constant of a reaction represented with a rate equation, rate = $k[A]^{1/2}\,[B]^{1/2}$
(a) mol^{-1} L s^{-1} (b) s^{-1}
(c) mol $L^{-1}s^{-1}$ (d) mol^{-2} L^2 s^{-1}
(e) mol^{-3} L^3 s^{-1}

46. Under what condition the order of reaction,

$$2HI_{(g)} \xrightarrow{\Delta,\ \text{catalyst}} H_{2(g)} + I_{2(g)},\ \text{is zero ?}$$

(a) At high temperature
(b) At high partial pressure of HI
(c) At low partial pressure of HI
(d) At high partial pressure of H_2
(e) At high partial pressure of I_2

47. Which of the following statements is true about the adsorption?
(a) $\Delta H < 0$ and $\Delta S < 0$
(b) $\Delta H > 0$ and $\Delta S < 0$
(c) $\Delta H < 0$ and $\Delta S > 0$
(d) $\Delta H = 0$ and $\Delta S < 0$
(e) $\Delta H = 0$ and $\Delta S > 0$

48. In NH_3 synthesis by Haber's process, what is the effect on the rate of the reaction with the addition of Mo and CO, respectively?
(a) Increases and decreases.
(b) Decreases and decreases.
(c) Decreases and increases.
(d) Both Mo and CO increases the rate.
(e) Both Mo and CO does not affect the rate.

SOLUTIONS

1. (c) : Ionisation enthalpy decrease down the group and increases from left to right in a period.
So, the order of increasing first ionisation potential is
Li < H < N < Ne < He

2. (d) : In principle, electrons are added one at a time to the penultimate d-orbitals but due to extra stability of d^5 and d^{10} configurations, two electrons appears to have entered the d-shell due to shifting of one electron from ns to $(n-1)d$ orbital.

3. (c) : Electronegativity generally increases on moving across a period from left to right and decreases from top to bottom in a group.
So, the correct order is

Si	<	P	<	C	<	N
1.9		2.19		2.5		3.0

4. (d) : Electronic configuration of
Gd(64) : [Xe] $4f^7$, $5d^1$, $6s^2$
So, total unpaired electrons = 8

$$\text{Sum of spin} = \frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2} = 4$$

5. (d) : $2SO_{2(g)} + Na_2CO_{3(aq)} + H_2O_{(l)} \rightarrow 2NaHSO_{3(aq)} + CO_{2(g)}$
$\downarrow Na_2CO_{3(aq)}$
$Na_2SO_{3(aq)} + H_2O_{(l)} + CO_{2(g)}$

Thus, both products $NaHSO_3$ and Na_2SO_3 are formed when SO_2 gas is passed through aqueous Na_2CO_3 solution.

6. (d) : Portland cement contains $CaSiO_4$, $CaSiO_3$ and $Ca_3Al_2O_6$ but not $Ca_3(PO_4)_2$.

7. (b) : Aluminium sulphate is mainly used as a coagulating agent in purification of drinking water and waste water treatment of plants, as mordant in dying and printing textile and also used in calico printing and sizing of paper industry.

8. (a) : Nitrogen does not have vacant d-orbitals so maximum number of covalent bonds it can form is 3 while phosphorus can form five covalent bonds due to presence of vacant d-orbitals.

9. (e)

10. (a) : $\left[:\ddot{O}-\ddot{O}:\right]^{2-}$ $\left[C\equiv O:\right]^{+}$ $\left[O\equiv O\right]^{+}$

O_2^{2-} CO^+ O_2^+

Thus, only O_2^{2-} have σ bonds alone.

11. (a) : Cl_2O and ClO_2 both gases are used to prepare $NaClO_2$, which is used as bleaching agent.

$$BrO_3^- + F_2 + 2OH^- \longrightarrow BrO_4^- + 2F^- + H_2O$$

12. (a) : H_2O_2 reduced acidified $K_2Cr_2O_7$.

$$\underset{\text{Oragne colour solution}}{K_2Cr_2O_{7(aq)}} + 4H_2SO_{4(aq)} + 3H_2O_{2(aq)} \longrightarrow K_2SO_{4(aq)} + \underset{\text{Green colour solution}}{Cr_2(SO_4)_{3(aq)}} + 7H_2O_{(l)} + 3O_{2(g)}$$

13. (a) : $(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} Cr_2O_3 + N_2 + 4H_2O$

$NH_4NO_2 \xrightarrow{\text{Heat}} N_2 + 2H_2O$

$2NH_4VO_3 \xrightarrow{\text{Heat}} V_2O_5 + 2NH_3 + H_2O$

$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$

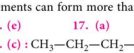
14. (b) : 

15. (d) : Carbon cannot form four bonds because of the absence of *d*-orbitals, cannot expand its valence shell beyond four and hence its maximum covalency or coordination number is four. However, Si, Ge, Sn and Pb due to the availability of vacant *d*-orbitals show a coordination of greater than 4 (*i.e.* 5 or 6). So, these elements can form more than four bonds.

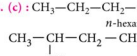
16. (e) **17. (a)**

18. (c) : $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

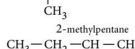
n-hexane



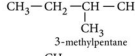
2-methylpentane



3-methylpentane

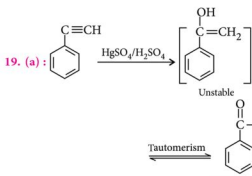


2,2-dimethylbutane

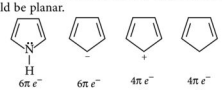


2,3-dimethylbutane

19. (a) :



20. (a) : According to Huckel rule, for a compound to be aromatic, it should contain $(4n + 2)\pi$ electrons and should be planar.

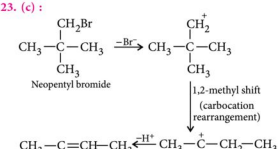


Thus, *A* and *B* are aromatic.

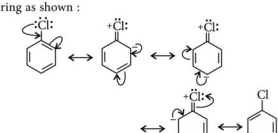
21. (c)

22. (c) : A molecule containing plane of symmetry cannot be optically active.

23. (c) :



24. (d) : In chlorobenzene, the lone pairs of electron on the chlorine atom are delocalised on the benzene ring as shown :



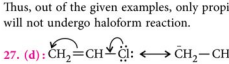
As a result, C – Cl bond acquires some double bond character, hence difficult to break or substitute.

25. (e) : Long chain alcohols are oxidised to aldehydes, most likely, which is a key reaction in the manufacture of perfumes.

26. (e) : For a compound to undergo haloform reaction it should have either $CH_3-\underset{\underset{O}{\|}}{C}-$ or $CH_3-\underset{\underset{OH}{|}}{CH}-$ group.

$CH_3-\underset{\underset{O}{\|}}{C}-H$, CH_3-CH_2-OH, $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

Acetaldehyde — Ethanol — Acetone



Acetophenone — Propiophenone

Thus, out of the given examples, only propiophenone will not undergo haloform reaction.

27. (d) : $\overset{\curvearrowleft}{CH_2}=CH-\ddot{\underset{\curvearrowright}{Cl}}: \longleftrightarrow \bar{C}H_2-CH=\overset{+}{Cl}:$

Thus, C—Cl bond acquires partial double bond character and will not undergo substitution.

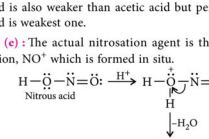
28. (a) : $CH_3-\underset{\underset{O}{\|}}{C}-O-OH$ Peroxyacetic acid; $CH_3-\underset{\underset{O}{\|}}{C}-OH$ Acetic acid

$Cl-CH_2-\underset{\underset{O}{\|}}{C}-OH$ Chloroacetic acid; $Cl-\underset{\underset{Cl}{|}}{\overset{Cl}{\overset{|}{C}}}-\underset{\underset{O}{\|}}{C}-OH$ Trichloroacetic acid

$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH$ Propanoic acid

Peroxyacetic acid is much weaker than acetic acid. While chloroacetic acid and trichloroacetic acid are stronger than acetic acid due to $-I$ effect. Propanoic acid is also weaker than acetic acid but peroxyacetic acid is weakest one.

29. (e) : The actual nitrosation agent is the nitrosyl cation, NO^+ which is formed in situ.



Nitrous acid — Nitrosonium ion

Aromatic tertiary amine *i.e.*, *N,N*-dimethyl aniline, undergo electrophilic substitution with nitrosonium ion at *p*-position of phenyl ring.

30. (d) **31. (a)**

32. (a) : Barbiturates is an important class of tranquillizers. They are used as hypnotics *i.e.*, sleep producing agents.

33. (a) : $2\overset{+2}{Fe}SO_4 \longrightarrow 2\overset{+3}{Fe}_2(SO_4)_3$

Change in oxidation state per Fe atom is 1. So, equivalent weight = atomic weight.

34. (a) : Ethanol is C_2H_5OH.

Molecular mass = $12 \times 2 + 6 \times 1 + 16 \times 1$
$= 24 + 6 + 16 = 46$

Mass of carbon in ethanol = $12 \times 2 = 24$

$$\text{Mass \% of carbon} = \frac{\text{Mass of carbon}}{\text{Molar mass of compound}} \times 100$$

$$= \frac{24}{46} \times 100 = 52\%$$

35. (b) : $2C_{(s)} + \frac{1}{2}O_{2(g)} + 3H_{2(g)} \rightarrow C_2H_5OH_{(l)}$:
$\Delta H_f = -277.7$ kJ mol^{-1}

By doubling the reaction,
$4C_{(s)} + O_{2(g)} + 6H_{2(g)} \rightarrow 2C_2H_5OH$;
$\Delta H_f = 2 \times -277.7 = -555.4$ kJ mol^{-1}

36. (c) **37. (b)** **38. (a)**

39. (c) : Molality of NaCl solution

$$= \frac{\text{Moles}}{\text{Mass of solvent (kg)}} = \frac{1}{1} = 1 \text{ m}$$

$\Delta T_b = iK_b m = 2 \times 0.52 \times 1 = 1.04$ K
$T_b = T_b^\circ + \Delta T_f = 373.15 + 1.04$
$= 374.19$ K

40. (None) : Net reaction of H_2-O_2 fuel cell :
$2H_2 + O_2 \rightarrow 2H_2O$

$$w = ZIt = \frac{EIt}{96500}$$

$$= \frac{9 \times 1 \times 595.1 \times 60 \times 60}{96500} = 200 \text{ g}$$

Density of water = 1 g/mL

$$M = \frac{\text{Moles of NaOH}}{200} \times 1000 = \frac{5 \times 1000}{40 \times 200} = 0.625 \text{ M}$$

41. (a) : $AgCl \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{Cl^-}$ ...(i)

$KCl \rightleftharpoons K^+ + Cl^-$ ...(ii)
$0.1 \quad 0.1$

$[Ag^+] = x$;

$[Cl^-] = x + 0.1 \qquad [\because\ x << 0.1]$

$\therefore\ [Cl^-] = 0.1$

$K_{sp} = [Ag^+]\,[Cl^-]$ (To just start the precipitation)

$x \times 0.1 = 1.8 \times 10^{-10}$

$$x = \frac{1.8\times10^{-10}}{0.1} = 1.8\times10^{-9}$$

Mass of AgCl(w) $= 1.8 \times 10^{-9} \times 143$

$w = ZIt$

$$t = \frac{w}{ZI} = \frac{1.8\times10^{-9}\times143\times96500}{143\times1\times10^{-6}} = 173.7 \text{ s}$$

42. (a) : $2Li_{(s)} + F_{2(g)} \longrightarrow 2LiF_{(aq)}$

$E^\circ_{cell} = 5.92$ V

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log[LiF]^2$$

$$E^\circ_{cell} = 5.92 - \frac{0.059}{2}\log 2^2$$

$= 5.92 - 0.059 \times 0.3010 = 5.90$

43. (a) : $\alpha = \dfrac{\text{Molar conductivity}}{\text{Limiting molar conductivity}}$

$$= \frac{240}{420} = \frac{12}{21}$$

$$\alpha = \frac{i-1}{n-1} = \frac{i-1}{2-1} = \frac{12}{21}$$

$$i = \frac{12}{21} + 1 = \frac{33}{21}$$

$$\Delta T_b = iK_b m = \frac{33}{21}\times0.52\times3 = 2.45 \text{ K}$$

$T_b = T_b^\circ + \Delta T_b = 373.15 + 2.45 = 375.6$ K

44. (a) : $A + D_2 \rightarrow$ Product

Suppose rate law expression for the reaction is

Rate $= k[D_2]^x\,[A]^y$

$1 \times 10^{-3} = k[0.05]^x\,[0.05]^y$ ...(i)

$3 \times 10^{-3} = k[0.15]^x\,[0.05]^y$ ...(ii)

$9 \times 10^{-3} = k[0.05]^x\,[0.15]^y$ ...(iii)

From equations (i) and (ii), we get

$$\frac{1\times10^{-3}}{3\times10^{-3}} = \frac{[0.05]^x}{[0.15]^x}$$

$$\frac{1}{3} = \frac{1}{3^x} \ \Rightarrow\ x = 1$$

From equations (i) and (iii), we get

$$\frac{1\times10^{-3}}{9\times10^{-3}} = \frac{(0.05)^y}{(0.15)^y}$$

$$\frac{1}{9} = \frac{1}{3^y} \ \Rightarrow\ y = 2$$

Thus, rate law expression is

Rate of reaction $= k[D_2]^1\,[A]^2$

45. (a) : Rate $= k[A]^{1/2}\,[B]^{3/2}$

$$k = \frac{\text{rate}}{[A]^{1/2}\,[B]^{3/2}} = \frac{\text{mol L}^{-1}\,\text{s}^{-1}}{[\text{mol L}^{-1}]^{1/2}\,[\text{mol L}^{-1}]^{3/2}}$$

$= \text{mol}^{-1}\,\text{L}\,\text{s}^{-1}$

46. (b)

47. (a) : During adsorption, there is always decrease in residual forces of the surface *i.e.*, there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably accompanied by evolution of heat *i.e.*, it is an exothermic process. In other words, ΔH of adsorption is always negative.

When a gas is adsorbed, the freedom of movement of its molecules becomes restricted. This causes decrease in the entropy of the gas after adsorption *i.e.*, ΔS is negative.

48. (a)

WBJEE SOLVED PAPER 2018

*Arunava Sarkar

CATEGORY-I (Q. 1 to Q. 30)

Carry-1 mark each and only one option is correct. In case of incorrect answer or any combination of more than one answer, 1/4 mark will be deducted.

1. Cl_2O_7 is the anhydride of
(a) HOCl (b) $HClO_2$
(c) $HClO_3$ (d) $HClO_4$

2. The main reason that $SiCl_4$ is easily hydrolysed as compared to CCl_4 is that
(a) Si – Cl bond is weaker than C – Cl bond
(b) $SiCl_4$ can form hydrogen bonds
(c) $SiCl_4$ is covalent
(d) Si can extend its coordination number beyond four.

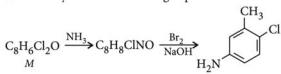
3. Silver chloride dissolves in excess of ammonium hydroxide solution. The cation present in the resulting solution is
(a) $[Ag(NH_3)_6]^+$ (b) $[Ag(NH_3)_4]^+$
(c) Ag^+ (d) $[Ag(NH_3)_2]^+$

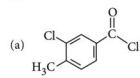
4. The ease of hydrolysis in the compounds : CH_3COCl (I), $CH_3CO-O-COCH_3$ (II), $CH_3COOC_2H_5$ (III) and CH_3CONH_2 (IV) is of the order
(a) I > II > III > IV (b) IV > III > II > I
(c) I > II > IV > III (d) II > I > IV > III

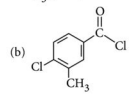
5. $CH_3-C\equiv CMgBr$ can be prepared by the reaction of
(a) $CH_3-C\equiv C-Br$ with $MgBr_2$
(b) $CH_3-C\equiv CH$ with $MgBr_2$
(c) $CH_3-C\equiv CH$ with KBr and Mg metal
(d) $CH_3-C\equiv CH$ with CH_3MgBr.

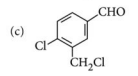
6. The number of alkene(s) which can produce 2-butanol by the successive treatment of (i) B_2H_6 in tetrahydrofuran solvent and (ii) alkaline H_2O_2 solution is
(a) 1 (b) 2 (c) 3 (d) 4

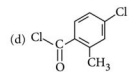
7. Identify '*M*' in the following sequence of reactions:



(a) 

(b) 

(c) 

(d) 

8. Methoxybenzene on treatment with HI produce
(a) iodobenzene and methanol
(b) phenol and methyl iodide
(c) iodobenzene and methyl iodide
(d) phenol and methanol.

9. $\underset{N}{C_4H_{10}O} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} C_4H_8O \xrightarrow[\text{warm}]{I_2/NaOH} CHI_3$

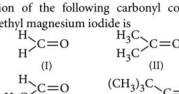
Here, *N* is

*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

(a)  (b) 

(c)  (d) 

10. The correct order of reactivity for the addition reaction of the following carbonyl compounds with ethyl magnesium iodide is



(I) (II) (III) (IV)

(a) I > III > II > IV (b) IV > III > II > I
(c) I > II > IV > III (d) III > II > I > IV

11. If aniline is treated with conc. H_2SO_4 and heated at 200 °C, the product is
(a) anilinium sulphate (b) benzenesulphonic acid
(c) *m*-aminobenzenesulphonic acid
(d) sulphanilic acid.

12. Which of the following electronic configuration is not possible?
(a) $n = 3, l = 0, m = 0$
(b) $n = 3, l = 1, m = -1$
(c) $n = 2, l = 0, m = -1$
(d) $n = 2, l = 1, m = 0$

13. The number of unpaired electrons in Ni (atomic number = 28) are
(a) 0 (b) 2 (c) 4 (d) 8

14. Which of the following has the strongest H-bond?
(a) O — H --- S (b) S — H --- O
(c) F — H --- F (d) F — H --- O

15. The half-life of C^{14} is 5760 years. For a 200 mg sample of C^{14}, the time taken to change to 25 mg is
(a) 11520 years (b) 23040 years
(c) 5760 years (d) 17280 years.

16. Ferric ion forms a prussian blue precipitate due to the formation of
(a) $K_4[Fe(CN)_6]$ (b) $K_3[Fe(CN)_6]$
(c) $Fe(CNS)_3$ (d) $Fe_4[Fe(CN)_6]_3$

17. The nucleus $^{64}_{29}Cu$ accepts an orbital electron to yield
(a) $^{65}_{28}Ni$ (b) $^{64}_{30}Zn$
(c) $^{64}_{28}Ni$ (d) $^{65}_{30}Zn$

18. How many moles of electrons will weigh one kilogram?
(a) 6.023×10^{23} (b) $\frac{1}{9.108} \times 10^{21}$
(c) $\frac{6.023}{9.108} \times 10^{54}$ (d) $\frac{1}{9.108 \times 6.023} \times 10^{8}$

19. Equal weights of ethane and hydrogen are mixed in an empty container at 25 °C. The fraction of total pressure exerted by hydrogen is
(a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16

20. The heat of neutralisation of a strong base and a strong acid is 13.7 kcal. The heat released when 0.6 mole HCl solution is added to 0.25 mole of NaOH is
(a) 3.425 kcal (b) 8.22 kcal
(c) 11.645 kcal (d) 13.7 kcal

21. A compound formed by elements *X* and *Y* crystallises in the cubic structure, where *X* atoms at the corners of a cube and *Y* atoms are at the centres of the body. The formula of the compound is
(a) *XY* (b) XY_2 (c) X_2Y_3 (d) XY_3

22. What amount of electricity can deposit 1 mole of Al metal at cathode when passed through molten $AlCl_3$?
(a) 0.3 F (b) 1 F (c) 3 F (d) 1/3 F

23. Given the standard half-cell potentials ($E°$) of the following as :

$Zn = Zn^{2+} + 2e^-$; $E° = +0.76$ V
$Fe = Fe^{2+} + 2e^-$; $E° = 0.41$ V

Then, the standard e.m.f. of the cell with the reaction $Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ is
(a) –0.35 V (b) +0.35 V
(c) +1.17 V (d) –1.17 V

24. The following equilibrium constants are given :

$N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1
$N_2 + O_2 \rightleftharpoons 2NO$; K_2

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$; K_3

The equilibrium constant for the oxidation of 2 mol of NH_3 to give NO is

(a) $K_1 \cdot \frac{K_2}{K_3}$ (b) $K_2 \cdot \frac{K_3^3}{K_1}$

(c) $K_2 \cdot \frac{K_3^2}{K_1}$ (d) $K_2^2 \cdot \frac{K_3}{K_1}$

25. Which one of the following is a condensation polymer?
(a) PVC (b) Teflon
(c) Dacron (d) Polystyrene

26. Which of the following is present in maximum amount in acid rain?
(a) HNO_3 (b) H_2SO_4
(c) HCl (d) H_2CO_3

27. Which of the set of oxides are arranged in the proper order of basic, amphoteric, acidic?
(a) SO_2, P_2O_5, CO (b) BaO, Al_2O_3, SO_2
(c) CaO, SiO_2, Al_2O_3 (d) CO_2, Al_2O_3, CO

28. Out of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one?
(a) $(n-1)\,d^8\,ns^2$ (b) $(n-1)\,d^5\,ns^2$
(c) $(n-1)\,d^3\,ns^2$ (d) $(n-1)\,d^5\,ns^1$

29. At room temperature, the reaction between water and fluorine produces
(a) HF and H_2O_2 (b) HF, O_2 and F_2O_2
(c) F^-, O_2 and H^+ (d) HOF and HF.

30. Which of the following is least thermally stable?
(a) $MgCO_3$ (b) $CaCO_3$
(c) $SrCO_3$ (d) $BeCO_3$

CATEGORY-II (Q. 31 to Q. 35)

Carry-2 marks each and only one option is correct. In case of incorrect answer or any combination of more than one answer, 1/2 mark will be deducted.

31. $[P] \xrightarrow{Br_2} C_2H_4Br_2 \xrightarrow[NH_3]{NaNH_2} [Q] \xrightarrow[Hg^{2+},\,\Delta]{20\%\ H_2SO_4} [R] \xrightarrow{Zn\text{-}Hg/HCl} [S]$

The species *P*, *Q*, *R* and *S* respectively are
(a) ethene, ethyne, ethanal, ethane
(b) ethane, ethyne, ethanal, ethene
(c) ethene, ethyne, ethanal, ethanol
(d) ethyne, ethane, ethene, ethanal.

32. The number of possible organobromine compounds which can be obtained in the allylic bromination of 1-butene with *N*-bromosuccinimide is
(a) 1 (b) 2 (c) 3 (d) 4

33. A metal *M* (specific heat 0.16) forms a metal chloride with a 65% chorine present in it. The formula of the metal chloride will be
(a) *M*Cl (b) MCl_2 (c) MCl_3 (d) MCl_4

34. During a reversible adiabatic process, the pressure of a gas is found to be proportional to the cube of its absolute temperature. The ratio $\frac{C_P}{C_V}$ for the gas is
(a) 3/2 (b) 7/2
(d) 5/3 (d) 9/7

35. $[X]$ + dil. $H_2SO_4 \rightarrow [Y]$ colourless suffocating gas
$[Y] + K_2Cr_2O_7 + H_2SO_4 \rightarrow$ green colouration of solution
Then, $[X]$ and $[Y]$ are
(a) SO_3^{2-}, SO_2 (b) Cl^-, HCl
(c) S^{2-}, H_2S (d) CO_3^{2-}, CO_2

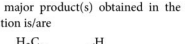
CATEGORY-III (Q. 36 to Q. 40)

Carry-2 marks each and one or more option(s) is/are correct. If all correct answers are not marked and also no incorrect answer is marked then score = 2 × number of correct answers marked ÷ actual number of correct answers. If any wrong option is marked or if any combination including a wrong option is marked, the answer will be considered wrong, but there is no negative marking for the same and zero marks will be awarded.

36. The possible product(s) to be obtained from the reaction of cyclobutyl amine with HNO_2 is/are

(a) 
(b) 
(c) 
(d) $H_2C{=}CH_2$

37. The major product(s) obtained in the following reaction is/are



(a) 
(b) 
(c) 
(d) 

38. Which statements are correct for the peroxide ion?
(a) It has five completely filled anti-bonding molecular orbitals.
(b) It is diamagnetic.
(c) It has bond order one.
(d) It is isoelectronic with neon.

39. Among the following, the extensive variables are
(a) H (enthalpy) (b) P (pressure)
(c) E (internal energy) (d) V (volume)

40. White phosphorus P_4 has the following characteristics.
(a) 6 P – P single bonds
(b) 4 P – P single bonds
(c) 4 lone pair of electrons
(d) P – P – P angle of 60°

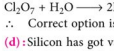
SOLUTIONS

1. **(d)** : In order to find out the corresponding acid of an anhydride, add water molecule (one mole) to the anhydride.
$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$
∴ Correct option is (d).

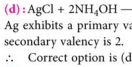
2. **(d)** : Silicon has got vacant 'd' orbital but carbon doesn't have that. Silicon, also has got larger size than carbon. Hence, silicon can have extended valency rather extended coordination number.
∴ Correct option is (d).

3. **(d)** : $AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]^+Cl^-$
Ag exhibits a primary valency of 1. So, tentative secondary valency is 2.
∴ Correct option is (d).

4. **(a)** : Concept :



So, in $CH_3-\overset{O}{\overset{\|}{C}}-Cl$; – Cl has good $-I$ effect and very little + R effect. So, the carbonyl carbon gets highly +ve charge.



atom is getting bifurcated. So, + R effect gets severely weaker and $-I$ effect shows dominance.

In $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}C_2H_5$ and $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$ nitrogen has got stronger + R effect than oxygen.
∴ Correct option is (a).

5. **(d)** : Acetylinic hydrogen is acidic and is replaceble. Grignard reagent (RMgBr) is ionised as shown below :
$\overset{-}{R}\,\overset{+}{M}gBr$ (due to appreciated electronegativity difference of carbon and magnesium).
So, the following reaction seems to be appreciable for the preparation of $CH_3-C\equiv CMgBr$.

$$CH_3-C\equiv\overset{\cdot\cdot}{\underset{+}{C}}H + CH_3\overset{+}{M}gBr \longrightarrow CH_3C\equiv\overset{\cdot\cdot}{\underset{+}{C}}MgBr + CH_4$$

∴ Correct option is (d).

6. **(b)** : Structure of butan-2-ol is :
$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$
Now, the simple format of HBO (hydroboration oxidation) reaction is :

$$R-CH=CH_2 + B_2H_6 \xrightarrow{THF} (RCH_2CH_2)_3B \xrightarrow[\bar{O}H]{H_2O_2} RCH_2CH_2\underset{OH}{\underset{|}{}}$$

So, $CH_3-CH=CH-CH_3$ definitely an option as the mechanistic approach for the BH_3 addition is as below :

$$CH_3-CH=CH-CH_3 \xrightarrow[(B_2H_6)]{BH_3}$$

$$CH_3-\overset{H\cdots\cdots BH_2}{\overset{\vdots}{CH}}=\overset{\vdots}{CH}-CH_3 \xrightarrow{2CH_3CH=CHCH_3} (CH_3CH_2-CHCH_3)_3B$$

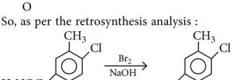
$$CH_3CH_2-\underset{OH}{\underset{|}{CHCH_3}} \xleftarrow[\bar{O}H]{H_2O_2}$$

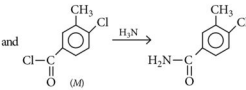
Now, $CH_3-CH=CH-CH_3$ can have both *cis* and *trans*-forms. So, correct option is (b).

7. **(b)** : Problem can be solved by using back reaction. we know,

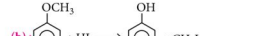
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{Hoffmann degradation reaction}]{Br_2/NaOH} R-NH_2$$

So, as per the retrosynthesis analysis :

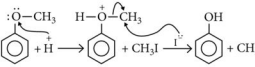


and 

∴ Correct option is (b).

8. **(b) :** 

Because,  is not stable at all. So, the reaction proceeds as shown below :



∴ Correct option is (b).

9. **(b) :** We should again use retrosynthesis analysis here,

As, $C_4H_8O \xrightarrow[\text{warm}]{I_2/NaOH} CHI_3$

So, C_4H_8O should have $-\overset{\overset{O}{\|}}{C}-CH_3$ group.

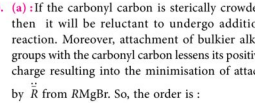
∴ $C_4H_8O - \overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow C_2H_5$

So, C_4H_8O can be $CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

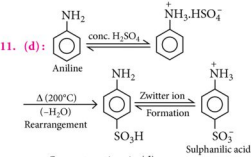
So, $C_4H_{10}O(N)$ should be $CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_3$

∴ Correct option is (b).

10. **(a) :** If the carbonyl carbon is sterically crowded then it will be reluctant to undergo addition reaction. Moreover, attachment of bulkier alkyl groups with the carbonyl carbon lessens its positive charge resulting into the minimisation of attack by $\overset{\cdot\cdot}{R}$ from *R*MgBr. So, the order is :

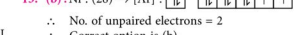


∴ Correct option is (a).

11. **(d) :** 

∴ Correct option is (d).

12. **(c) :** Option (c) is correct because for *l* to be zero, *m* can't be –1, because,
$m = -l$ to $+l$

13. **(b) :** Ni : (28) → [Ar] : 

∴ No. of unpaired electrons = 2
∴ Correct option is (b).

14. **(d) :** If the atom is neutral, electronegativity appears to be low and F^- is the conjugate base of HF. It will weaken the bond rather than H — O^-.
So the strongest H-bond is F — H ···· O

15. **(d) :** R_0 = 200 mg ; *R* = 25 mg ; $t_{1/2}$ = 5760 years
Suppose required years are *x*.
Also, suppose no. of half lives = *n*

$$\therefore \left(\frac{R}{R_0}\right)=\left(\frac{1}{2}\right)^n \Rightarrow \left(\frac{25}{200}\right)=\left(\frac{1}{2}\right)^n$$

$$\Rightarrow \left(\frac{1}{8}\right)=\left(\frac{1}{2}\right)^n \Rightarrow \left(\frac{1}{2}\right)^3=\left(\frac{1}{2}\right)^n$$

$\therefore n = 3$

$$\therefore n=\frac{x}{5760} \Rightarrow 3=\frac{x}{5760}$$

$\Rightarrow x = 5760 \times 3 = 17280$ years
∴ Correct option is (d).

16. **(d) :** Prussian blue precipitate is $Fe_4[Fe(CN)_6]_3$
∴ Correct option is (d).

17. **(c) :** $^{64}_{29}Cu + e^- \text{ (}k\text{-electron capture)} \longrightarrow {}^{64}_{28}Ni$
∴ Correct option is (c).

18. **(d) :** Mass of an electron = 9.108×10^{-31} kg
Mass of one mole of electron
$= 9.108 \times 10^{-31} \times 6.023 \times 10^{23}$
$= 9.108 \times 6.023 \times 10^{-8}$
∴ In 1 kg no. of moles of electrons

$$= \frac{1}{9.108\times 6.023\times 10^{-8}} = \frac{10^8}{9.108\times 6.023}$$

∴ Correct option is (d).

19. **(d)** : $M_{C_2H_6} = 30 ; M_{H_2} = 2$

Suppose, w is the weight of each of C_2H_6 and H_2 taken.

$$\therefore \quad n_{C_2H_6} = \frac{w}{30} ; n_{H_2} = \frac{w}{2}$$

$$\therefore \quad p_{H_2} = x_{H_2} \times p = \frac{n_{H_2}}{n_{H_2} + n_{C_2H_6}} \times p$$

$$\Rightarrow \quad p_{H_2} = \left(\frac{w/2}{\frac{w}{2} + \frac{w}{30}}\right) p = \left(\frac{1/2}{\frac{1}{2} + \frac{1}{30}}\right) p$$

$$\Rightarrow \quad p_{H_2} = \frac{15}{16} p \Rightarrow p_{H_2} : p = 15 : 16$$

$\therefore$ Correct option is (d).

20. **(a)** : For the neutralization between a strong acid and a strong base, equal number of moles of H^+ (from acid) and $\bar{O}H$ (from base) come out. For one mole of such, following equation can be drawn :

$$\overset{+}{H} + \bar{O}H \longrightarrow H_2O$$

At $t = 0$,	0.6	0.25	
After reaction	(0.6 – 0.25) = 0.35	0	0.25

So, 0.25 mole of H_2O is produced.

$\therefore$ Heat released = (0.25 × 13.7) kcal
= 3.425 kcal

$\therefore$ Correct option is (a).

21. **(a)** : $X = \left(8 \times \frac{1}{8}\right) = 1 ; Y = 1$

$\therefore$ Formula = XY

$\therefore$ Correct option is (a).

22. **(c)** : $Al^{3+} + 3e \longrightarrow Al$

1 mole electrons ≡ Faraday change

$\therefore$ 3 moles electrons ≡ 3 Faraday change

$\therefore$ Correct option is (c).

23. **(b)** : $Fe^{2+} + Zn \longrightarrow Fe + Zn^{2+}$

$\therefore$ Standard EMF of the cell
= Oxidation potential of anode + Reduction potential of cathode
= (0.76) + (–0.41) = 0.35 V

$\therefore$ Correct option is (b)

24. **(b)** : $N_2 + 3H_2 \rightleftharpoons 2NH_3 ; K_1$

$$K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$N_2 + O_2 \rightleftharpoons 2NO ; K_2$

$H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O ; K_3$

$$K_2 = \frac{[NO]^2}{[N_2][O_2]} ; \qquad K_3 = \frac{[H_2O]}{[H_2][O_2]^{1/2}}$$

Now, oxidation of NH_3 takes places as below :

$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$

or $2NH_3 + \frac{5}{2} O_2 \rightleftharpoons 2NO + 3H_2O$

(this is asked in the question)

$$K = \frac{[NO]^2 [H_2O]^3}{[NH_3]^2 [O_2]^{5/2}}$$

$$K = \frac{[NO]^2}{[N_2][O_2]} \cdot \frac{[N_2][O_2]}{[NH_3]^2} \cdot \frac{[N_2][H_2]^3}{[N_2][H_2]^3} \cdot \frac{[H_2O]^3}{[H_2]^3[O_2]^{3/2}} \cdot \frac{[H_2]^3[O_2]^{3/2}}{[O_2]^{5/2}}$$

$$= \left\{\frac{[NO]^2}{[N_2][O_2]}\right\} \cdot \left\{\frac{[N_2][H_2]^3}{[NH_3]^2}\right\} \cdot \left\{\frac{[H_2O]^3}{[H_2]^3[O_2]^{3/2}}\right\}$$

$$= K_2 \cdot \frac{1}{K_1} \cdot K_3^3 = \frac{K_3^3 K_2}{K_1}$$

$\therefore$ Option (b) is correct.

25. **(c)** : Dacron is a condensation polymer.

$\therefore$ Correct option is (c).

26. **(b)** : H_2SO_4 is found to be maximum in acid rain.

$\therefore$ Correct option is (b).

27. **(b)** : $BaO \rightarrow$ Basic ; $Al_2O_3 \rightarrow$ Amphoteric ; $SO_2 \rightarrow$ (acidic)

$\therefore$ Correct option is (b).

28. **(b)** : $(n-1)d^5\, ns^2$ can give +7 oxidation state.

$\therefore$ Correct option is (b).

29. **(c)** : $H_2O_{(l)} + F_{2(g)} \longrightarrow HF_{(aq)} + O_2$
$\downarrow$
$H^+_{(aq)} + F^-_{(aq)}$

$\therefore$ Correct option is (c).

30. **(d)** : $BeCO_3$ is least thermally stable. We know, for the alkaline earth metal carbonates, thermal stability order is
$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

$\therefore$ Correct option is (d)

31. (a) : $[P] \xrightarrow{Br_2} C_2H_4Br_2 \xrightarrow[NH_3]{NaNH_2} Q \xrightarrow[Hg^{2+},\,\Delta]{20\%\ H_2SO_4} R \xrightarrow[HCl]{Zn\text{-}Hg} S$

P is undergoing Br_2 addition reaction and Br_2 being used in 1 mol.

$\therefore \quad P = C_2H_4\ (CH_2=CH_2)$

$$H_2C{=}CH_2 + Br_2 \xrightarrow[\text{addition}]{\text{anti}} \underset{\underset{Br}{|}}{CH_2}{-}\underset{\underset{Br}{|}}{CH_2}$$
(P)

$$\xrightarrow[E_2]{\overset{+}{N}aNH_2/NH_3} HC{\equiv}CH \xrightarrow[Hg^{2+},\,\Delta]{20\%\ H_2SO_4}$$
(Q)

Elimination (twice) — Hydration reaction

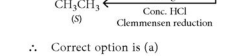
$$CH_2{=}CH \underset{OH}{|} \xrightleftharpoons{\text{Tautomerism}} CH_3{-}\overset{\overset{O}{\|}}{C}{-}H \quad (R)$$

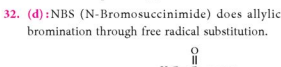
$$CH_3CH_3 \xleftarrow[\text{Conc. HCl}]{Zn\text{-}Hg} (S)$$

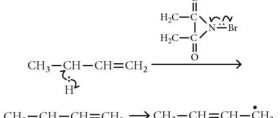
Clemmensen reduction

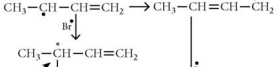
$\therefore$ Correct option is (a)

32. (d) : NBS (N-Bromosuccinimide) does allylic bromination through free radical substitution.









$\therefore$ Total 4 isomers are possible.

$\therefore$ Correct option is (d).

33. (b) : According to Dulong-Petit's law :

Approx at. mass × sp. heat = 6.4 (actually 6.4 ± 0.6)

$$\therefore \quad \text{At. mass (approx)} = \frac{6.4}{0.16} = 40$$

Suppose, formula of the chloride = MCl_x

$$\therefore \quad \text{Chloride in it} = \frac{35.5x \times 100}{40+35.5x}\,\%$$

So, according to the question,

$$\frac{35.5x}{40+35.5x} = \frac{65}{100} \Rightarrow \frac{40}{35.5x} + 1 = \frac{100}{65}$$

$$\Rightarrow \frac{40}{35.5x} = \frac{35}{65} = \frac{7}{13} \Rightarrow 35.5x = \frac{40 \times 13}{7}$$

$$\Rightarrow \quad x = 2.09 \approx 2$$

$\therefore$ Formula of the metal chloride $= MCl_2$

$\therefore$ Correct option is (b)

34. (a) : According to the question,

$P \propto T^3$ or $P = kT^3 \Rightarrow P.T^{-3} = k$ ...(i)

Now, for reversible adiabatic process

We have, $T^{\gamma}.P^{1-\gamma} = k$ ...(ii)

$$\Rightarrow \quad T^{\frac{\gamma}{1-\gamma}}.P = k \qquad \text{...(iii)}$$

Compare (i) and (iii), we get

$$\frac{\gamma}{1-\gamma} = -3 \Rightarrow \gamma = \frac{3}{2}$$

$\therefore$ Correct option is (a).

35. (a) : $\underset{\text{'X'}}{SO_3^{2-}}$ + dil. $H_2SO_4 \longrightarrow \underset{\text{'Y'}}{SO_2} + H_2O + SO_4^{2-}$

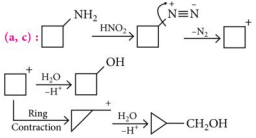
Green colouration on reaction with $K_2Cr_2O_7$ and H_2SO_4 shows that Y is SO_2.

$$\underset{\text{'Y'}}{K_2Cr_2O_7} + H_2SO_4 + 3SO_2 \longrightarrow \underset{\text{(Green colour)}}{Cr_2(SO_4)_3} + K_2SO_4 + H_2O$$

This confirms X is SO_3^{2-} ion and Y is SO_2 which is colourless suffocating gas.

$\therefore$ Correct option is (a).

36. (a, c) :



$\therefore$ Correct options are (a), (c).

37. (a, d) :

Br_2 addition is anti-addition.

Now remember 'CAR' and 'TAM' Rule.

C $\rightarrow$ Cis T $\rightarrow$ Trans

A $\rightarrow$ Anti A $\rightarrow$ Anti

R $\rightarrow$ Racemic M $\rightarrow$ Meso

$\therefore$ Correct options are (a), (d).

38. (b, c) : O_2^{2-} (18) : $(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* p_x)^2\ (\pi^* 2p_y)^2$

$\therefore$ No unpaired electrons = diamagnetic.

Bond order $= \frac{10-8}{2} = 1$

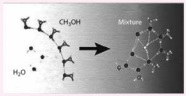
$\therefore$ Correct options are (b), (c).

39. (a, c, d)

40. (a, c, d) :

3 AMAZING FACTS ABOUT CHEMISTRY

1. When you step inside a bath tub, the water level will immediately go up, as per Archimedes' law. But when you add a volume of sodium chloride (salt) to a volume of water, the overall volume actually decreases by up to 2%. The net reduction in observed volume is due to solvent molecules which become more ordered in the vicinity of dissolved ions.



2. If you mix half a litre of alcohol and half a litre of water, the total volume of the liquid will be less than one litre.

When water and methyl alcohol mix, several forces come into play. First, between the water and methyl alcohol is strong hydrogen bonding that draws the different molecules close together. Second, open spaces in the liquid are much less likely because the methyl alcohol interferes with any temporary open structures that are similar to those of solid water. The two different molecules pack closer together than in pure solution, resulting in a reduction of volume.

3. One inch of rain is equal to 10 inches of snow

When the temperature is around 30 degrees F, one inch of liquid precipitation would fall as 10 inches of snow. The ratio of snow to water can vary a great deal depending on vertical profiles of temperature and moisture, and how they change during a storm. A typical ratio is 10 inches of snow per inch of water, but when the snow is wet, or mixes with freezing rain or sleet at times, the ratio may be much lower, around 3-5 inches for an inch of water. Conversely, on very rare occasions we get snow with a very cold atmospheric column, and in those cases there can be as much as 15-20 inches of snow per inch of liquid water.

CHEMISTRY MUSING

SOLUTION SET 58

1. (c) : Assume weight of bulb = w'

Wt. of air in bulb (w) = (22.567 – w')g

Pressure of air = $\frac{755}{760}$ atm

Volume of air = $\frac{200}{1000}$ litre

T = 293 K

Mol.wt. of air = 0.00129 × 22400 = 28.90 g

Using, $PV = \frac{w}{m}RT$ for air

$$\frac{755}{760} \times \frac{200}{1000} = \frac{(22.567 - w')}{28.90} \times 0.0821 \times 293$$

$\therefore \quad w'$ = 22.3282 g

Wt. of vapours = 22.8617 – 22.3282

= 0.5335 g

$$P_{vapour} = \frac{755}{760} \text{ atm}$$

Volume of vapours = 200 mL

T = 393 K

Again by, $PV = \frac{w}{m}RT$

$$\frac{755}{760} \times \frac{200}{1000} = \frac{0.5335}{m} \times 0.0821 \times 393$$

m = 86.64 u

2. (a) : (1) (C) is β-keto acid and thus, it may be,

$$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{R'}{|}}{CH}-COOH$$

(2) (C) on decarboxylation gives 3-pentanone, *i.e.*,

$$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{R'}{|}}{CH}-COOH \xrightarrow{\text{Soda lime}} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{R'}{|}}{CH_2}$$

$$\text{or } CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH_2}$$

3-Pentanone

Thus, R is $-C_2H_5$ and R' is $-CH_3$ group

$\therefore \quad$ (C) is $C_2H_5COCHCOOH$ (CH$_3$ branch)

(3) (C) is formed along with ethanol from (B) on acid hydrolysis, so (B) is a β-keto ester (ethyl ester).

$C_2H_5COCHCOOC_2H_5$ (CH$_3$ branch) —HOH→

(B)

$C_2H_5COCHCOOH + C_2H_5OH$ (CH$_3$ branch)

(C) Ethanol

2-Methyl-3-oxopentanoic acid

(4) (B) is formed as a condensation of two moles of ester (A), since the condensation occurs at 'α' C-atom, *i.e.*, Claisen condensation or Claisen reaction so, the probable formula of (A) is

$CH_3CH_2COOC_2H_5$

(A)

Reaction :

α-carbon

$2CH_3\underset{\text{Ethyl propanoate}}{CH_2COOC_2H_5} \xrightarrow{C_2H_5\bar{O}Na}$

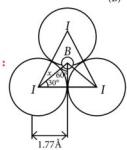
(A)

$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}COOC_2H_5 + C_2H_5OH$$

Ethyl-2-methyl-3-oxopentanoate

(B)

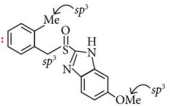
3. (c) :



$$x = \frac{1.77}{\sin 60^\circ} = 2.04 \text{ Å}$$

r_B = (2.04 Å) – (1.33 Å) = 0.71 Å

4. **(c) :**



5. **(c)** : By Gibbs-Helmholtz equation,

$$\Delta G^\circ = \Delta H^\circ + T\left[\frac{d(\Delta G^\circ)}{dT}\right]_p$$

$$\frac{\Delta G^\circ - \Delta H^\circ}{T} = \left[\frac{d(\Delta G^\circ)}{dT}\right]_p$$

But $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\therefore \quad -\Delta S^\circ = \left[\frac{d\Delta G^\circ}{dT}\right]_p$$

But $\Delta G^\circ = -nFE^\circ_{cell}$

$$\therefore \quad -\Delta S^\circ = -nF\left(\frac{dE^\circ_{cell}}{dT}\right)_p$$

$\left(\frac{dE^\circ_{cell}}{dT}\right)_p$ represents variation of e.m.f. of a cell with temperature. It is called temperature coefficient of e.m.f. of a cell.

$$\therefore \quad \left(\frac{dE^\circ_{cell}}{dT}\right)_p = \frac{\Delta S^\circ}{nF} = \frac{94.6\ \text{J K}^{-1}\text{mol}^{-1}}{2 \times 96500\ \text{C mol}^{-1}}$$

$$\therefore \quad \left(\frac{dE^\circ_{cell}}{dT}\right)_p = 4.9 \times 10^{-4}\ \text{V K}^{-1}$$

6. **(d)** : $A = Hg_2^{2+}$, $B = Hg_2CrO_4$
$C = Hg$, $D = Hg(NH_2)X$, $E = Hg_2I_2$
$F = Hg$, $G = [HgI_4]^{2-}$
Anionic part of 'B' is CrO_4^{2-}.

7. **(a)** : $h_L d_L = h_{Hg} d_{Hg}$

$$h_L = \frac{76 \times 13.6}{5.44} = 190\ \text{cm}$$

8. **(b)** : $P_{Gas} = P_{atm} + P_L = 1 + \frac{38}{180} = 1.2$

	$3A_{(g)}$	$\rightleftharpoons$	$A_{3(g)}$
$t = 0$	1.2 atm		0
$t = t_{eq}$	1.2 – 0.36		$\frac{1}{3}(0.36) = 0.12$ atm

$P_T = 1.2 - 0.36 + 0.12 = 0.96$ atm
Pressure difference in column = 1 – 0.96 = 0.04 atm
$\therefore$ The difference in height of the liquid level in two columns = 0.04 × 190 = 7.6 cm

9. **(2)** : For showing given reactions, compound should have :
(1) acidic H(—OH group)
(2) —CH—CH_3 group (to show iodoform test)
|
OH
(3) Secondary alcohol
Hence, structural isomers of $C_5H_{12}O$ which can satisfy these conditions are :

$CH_3—CH_2—CH_2—CH—CH_3$
|
OH

$CH_3—CH—CH—CH_3$
| |
H_3C OH

10. **(6)** : $[Cr(H_2O)_5Cl]Cl_2 + 2AgNO_3 \longrightarrow 2AgCl + [Cr(H_2O)_5Cl](NO_3)_2$
Number of ionizable Cl^- ions in the complex = 2
Millimoles of Cl^- ions = Molarity × volume × 2
= 0.01 × 30 × 2 = 0.6
Therefore, Ag^+ required for complete precipitation of Cl^- ions = 0.6 millimoles
As Millimoles = Molarity × V mL
0.6 = 0.1 × V mL
V = 6 mL

PUZZLE CORNER
SOLUTION - MAY 2018

1	2	3	4	5
3	4	1	5	2
4	1	5	2	3
2	5	4	3	1
5	3	2	1	4

(a) Magnesium (1 × 3 × 4 = 12)
(b) Flourine (2 + 3 + 4 = 9)
(c) Tin (5 × 5 × 2 = 50)
(d) Boron (1 × 5 = 5)
(e) Calcium (4 × 1 × 5 = 20)
(f) Argon (2 × 3 × 3 × 1 = 18)
(g) Zinc (2 × 5 × 3 = 30)
(h) Helium (4 – 2 = 2)
(i) Berylium (1 × 4 = 4)

Solution Senders of Chemistry Musing
Set - 58
- Nikhil Bohra, Uttar Pradesh
- Sunita Dutta, West Bengal

Winners of Chemdoku
- Nischay Paul, West Bengal
- Mitali Sharma, Haryana

ADVANCED CHEMISTRY BLOC

Mukul C. Ray, Odisha

INTRAMOLECULAR REACTIONS

Steps move towards lower free energy in the microscopic world of chemical reactions. In this context, entropy has its own contribution. Why a rubber band moves back and forth, though not in a regular rhythm? It has very weak intermolecular forces, rather say very weak forces operating between polymeric fibres in a rubber band. It's an elastomer. In elastomers, entropy is more favoured than enthalpy. It likes to remain in its original random conformation favoured by entropy. Similarly, intramolecular reactions are favoured by entropy. A single molecule reacts to produce two or higher number of fragments thereby contributing towards the feasibility of the process.

Intramolecular reactions may involve oxidation-reduction. On heating some substances, a powerful oxidising agent within the substance gets enough activation energy to reduce some other component of the same substance.

$$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + NO_2 + O_2$$

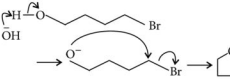
'Pb' due to inert pair effect is maintaining its +2 state but it is the 'N' which is an oxidising agent. Though, this reaction can be classified as thermal decomposition but we can also classify it as intramolecular redox reaction. You fix a 'basis' to classify the things. When you change the basis, things emerge in a different way. That is why you have so many ways of classifying the things.

Another similar example is

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + H_2O$$

In a similar way, a number of other thermal decompositions may be included. Keeping them aside, we can move to organic chemistry to see some interesting intramolecular reactions.

Generally, you never say alcohol is enough acidic to react with NaOH. But when you say you actually mean, the acid-base reaction between alcohol and NaOH is not a product favoured equilibrium. Few molecules of alcohol may loose proton which may pave the path of reaction. It's surely worth noting "Less frequent molecular collisions may decide the fate of molecule in some reactions".

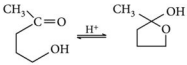


Look at the loss and gain. The random conformations of the open chain reactant is now lost. A ring cannot have so many conformations as open chain compound. Again, two fragments are formed, an ether and a Br^- ions. There is gain in entropy, which is strong enough to overpower the loss in entropy due to loss in conformations. But what if the upcoming ring is a six-membered one? Naturally, you have a longer open chain compound as starting material and you are likely to loose more random conformations during cyclisation. This may not be an encouraging situation and this is indeed true. "Rate constant for ring closing reaction is higher for five membered ring than six membered ring".

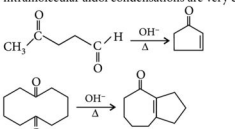
Another important parameter is "probability of ring closing". It's easy to fold a smaller chain into a ring than a longer chain. Probability of ring closing is therefore highest for three membered ring formation. But as you know, a three membered ring is under heavy strain. Therefore, ring closing reactions roughly proceed at the rate :

5 > 6; 3 > 4

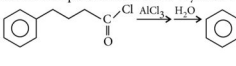
Loss of entropy due to cyclisation, probability of ring closing and ring strain together decide this trend and moreover intramolecular ring closing is favoured over intermolecular reactions.



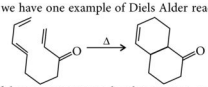
It's an intramolecular hemiacetal formation. Similarly, intramolecular aldol condensations are very common.



See an example of Friedel-Crafts' acylation :



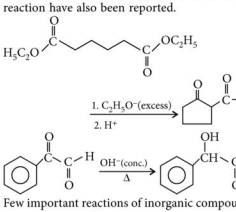
Here, we have one example of Diels Alder reaction :



A useful inorganic intramolecular reaction is :

$$\underset{\text{Adduct}}{BH_3.NH_3} \xrightarrow{200\ ^\circ C} B_3N_3H_6 + H_2$$

Intramolecular Claisen condensation, Cannizzaro reaction have also been reported.



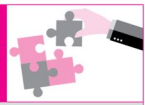
Few important reactions of inorganic compounds are :

$$MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgO + HCl + H_2O$$

$$ZnCl_2 \cdot 2H_2O \xrightarrow{\Delta} ZnO + HCl + H_2O$$

H_2O present in the compound hydrolyses the chloride to form hydroxide, which subsequently decomposes to give oxide.

PUZZLE CORNER



CHEMDOKU

In this puzzle 6 × 6 grid is given, your objective is to fill the digits 1-6 so that each appear exactly once in each row and each column.

Notice that most boxes are part of a cluster. In the upper-left corner of each multibox cluster is a value that is addition, subtraction or multiple (as indicated) of its numbers. For example, if that value is 3× for a two-box cluster, you know that only 1 and 3 can go in there. But it is your job to determine which number goes where! A few cluster may have just one box and that is the number that fills that box.

Note : Atomic masses of the given elements to be considered as your answer.

Clues :

(a) In gaseous form it is used as a blanketing gas and in liquid form it is used as a refrigerant to freeze foods, soft or rubbery materials.

(b) It is a silvery white lustrous metal, which is obtained by electrolysis of its chloride or fluoride. It is used for removing sulphur from petroleum and also to remove traces of water from alcohol.

a+			b×		
c+		d×			e+
f−	g×			h×	
		i+			
	j+				

(c) A very important element, which when mixed in liquid form with finely divided carbon, acts like dynamite in coal mining.

(d) It is a toxic silvery metal which occurs as mineral monazite and used to produce special dark glasses.

(e) This noble gas remains unadsorbed on charcoal even at –180 °C when mixture of noble gases brought in contact.

(f) It was first liquefied by James Dewar in 1898 by using regenerative cooling and vacuum flask and next year he produced its solid form.

(g) One of its isotope has half life 5.7×10^3 years and constantly being produced by reaction between cosmic ray neutrons and nitrogen in upper atmosphere.

(h) It is a silvery-yellow metal, used in permanent magnets and in conjunction with other compounds it is used to kill cancer cells.

(i) It is non-metallic, extremely hard (very strong crystalline lattice) coloured solid. Its pure form is obtained from reduction or pyrolysis of its halides.

(j) Its batteries are used wherever a reliable current is required for a lengthy period. Pacemaker battery is an example of this type of batteries.

Readers can send their responses at editor@rmtg.in or post us with complete address. Solution Senders name with their valuable feedback will be published in next issue. Hope our readers will enjoy solving Chemdoku.

CLASS XII

CBSE DRILL

Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2018-19.

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 12 are short answer questions and carry 2 marks each.
(iv) Q. no. 13 to 24 are also short answer questions and carry 3 marks each.
(v) Q. no. 25 to 27 are long answer questions and carry 5 marks each.
(vi) Use log tables if necessary, use of calculator is not allowed.

Time Allowed : 3 hours

Maximum Marks : 70

Solid State | Solutions

1. A solid *AB* has NaCl structure. If the radius of the cation A^+ is 120 pm, calculate the maximum possible value of the radius of the anion *B*.

2. What happens to vapour pressure of water, if a tablespoon of glucose is added to it?

3. Name the type of point defect that occurs in a crystal of zinc sulphide.

4. Define azeotropic mixture.

5. Identify the crystal systems which have the following crystallographic dimensions.
(i) $a = b \neq c$; $\alpha = \beta = \gamma = 90°$
(ii) $a = b \neq c$; $\alpha = \beta = 90°, \gamma = 120°$

6. The vapour pressure of pure benzene at a certain temperature is 640 mmHg. A non-volatile, non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mmHg. What is the molecular mass of solid substance?

7. What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?

8. Calculate the normality and molarity of H_2SO_4 in a solution containing 9.8 g of H_2SO_4 per dm^3 of the solution.

9. A metal crystallises into two cubic phases, face centred cubic (*fcc*) and body centred cubic (*bcc*) whose unit cell lengths are 3.5 Å and 3.0 Å respectively. Calculate the ratio of densities of *fcc* and *bcc*.

10. The HCl used in the laboratory is 21.3% (*w*/*v*). What is its molarity?

OR

Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of a 0.15 M solution in methanol.

11. Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.
(i) What is the length of the side of the unit cell?
(ii) How many unit cells are there in 1.00 cm^3 of aluminium?

12. The freezing point depression of 0.1 molal solution of acetic acid in benzene is 0.256 K. K_f for benzene

is 5.12 K kg mol^{-1}. What conclusion can you draw about the molecular state of acetic acid in benzene?

13. How will you distinguish between the following pairs of terms :
- **(i)** Hexagonal close packing and cubic close packing
- **(ii)** Crystal lattice and unit cell
- **(iii)** Tetrahedral void and octahedral void

14. **(i)** What is osmotic pressure?
- **(ii)** A solution containing 4 g of a non-volatile organic solute per 100 cm^3 was found to have an osmotic pressure equal to 500 cmHg, at 27 °C. Calculate the molar mass of the solute.

15. **(i)** In the crystal structure of the mineral perovskite, Ca^{2+} ion is at the body-centre, Ti^{4+} ions are at the corners and O^{2-} ions at the edge-centres of a cubic unit cell. What is the formula unit of perovskite?
- **(ii)** A cubic solid is made of two elements *P* and *Q*. The atoms of *Q* are at the corners of the cube and an atom of *P* lies at the body-centre. What is the formula of the compound? What are the coordination numbers of *P* and *Q*?

16. A bottle of commercial sulphuric acid (density = 1.787 g/mL) is labelled as 86 percent by weight.
- **(i)** What is the molarity of the acid?
- **(ii)** What volume of the acid has to be used to make 1 L of 0.2 M H_2SO_4?
- **(iii)** What is the molality of the acid?

17. **(i)** LiI occurs as cubic close packing. If the edge length of a unit cell is 624 pm, determine the ionic radii of Li^+ and I^- ions.
- **(ii)** Lithium forms body-centred cubic crystals. Calculate the atomic radius of lithium if the length of the side of a unit cell of lithium is 351 pm.

18. Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa, respectively. What will be the vapour pressure, in bar, of a mixture of 25.0 g of heptane and 35.0 g of octane?

19. **(i)** Explain the following terms with one suitable example of each.
  - **(a)** Ferromagnetism
  - **(b)** Paramagnetism
- **(ii)** Give reason :
  Ferrimagnetic substances show better magnetism than antiferromagnetic substances.

20. *A* and *B* are two miscible liquids whose vapour pressures are 450 mmHg and 375 mmHg, respectively at a certain temperature. They are mixed in equimolar proportions.
- **(i)** What is the total vapour pressure over the liquid mixture at equilibrium?
- **(ii)** What is the mole fraction of *A* in the vapour?
- **(iii)** How many moles of *B* should be mixed with 1 mol of *A* for the vapour to be equimolar in *A* and *B*?

21. Answer the following :
- **(i)** Some of the glass objects, recovered from ancient monuments, look milky instead of being transparent. Why?
- **(ii)** Write any two differences between amorphous solids and crystalline solids.

OR

The density of crystalline sodium chloride is 2.165 g cm^{-3}. What is the edge length of the unit cell. What would be the dimensions of cube containing one mole of NaCl?

22. **(i)** A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution.
- **(ii)** If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water. Assume that N_2 exerts a partial pressure of 0.987 bar. The K_H for N_2 at 293 K is 76.48 k bar.

23. **(i)** What are non-stoichiometric defects?
- **(ii)** What fraction of iron atoms is present as Fe(III) in $Fe_{0.96}O$?

24. **(i)** The unit cell cube length for LiCl (NaCl type structure) is 5.14 Å. Assuming anion-anion contact, calculate the ionic radius for chloride ion.
- **(ii)** How many unit cells are present in 39 g of potassium that crystallises in body-centred cubic structure?
- **(iii)** A soda water bottle was opened and the soft drink is allowed to come at 27 °C with the air containing carbon dioxide at 3.8×10^{-4} atm. What would be the concentration of carbon dioxide in the soda water after it has left open and come to equilibrium. Give value of Henry's

constant for aqueous solution of carbon dioxide at 26 °C is 3.1×10^{-2} mol L^{-1} atm^{-1}.

25. (i) Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water? (a) phenol, (b) toluene, (c) formic acid, (d) ethylene glycol, (e) chloroform, (f) pentanol.

(ii) Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose to nalorphene generally given is 1.5 mg. Calculate the mass of 1.5×10^{-3} m aqueous solution required for the above dose.

OR

(i) The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given below. Explain briefly.

Trifluoroacetic acid > trichloroacetic acid > acetic acid

(ii) Upon heating a litre of a N/2 HCl solution, 2.675 g hydrogen chloride is lost and the volume of the solution shrinks to 750 mL. Calculate

(i) the normality of the resultant solution and

(ii) the number of milliequivalents of HCl in 100 mL of the original solution.

26. (i) At 1425 °C, Fe crystallises in a body-centred cubic lattice whose edge length is 2.93 Å. Assuming the atoms to be packed spheres, calculate

(a) the radius of the spheres,

(b) the distance between centres of neighbouring spheres and

(c) the number of atoms of Fe per unit lattice.

(ii) If NaCl is doped with 10^{-3} mol % of $SrCl_2$, what is the concentration of cation vacancy?

OR

(i) What is a semiconductor? Describe the two main types of semiconductors and their conduction mechanism.

(ii) Calcium crystallises in face-centred cubic unit cell with $a = 0.556$ nm. Calculate density if

(a) it contained 0.1% Frenkel defect.

(b) it contained 0.1% Schottky defect.

27. (i) What are colligative properties? Give two examples.

(ii) 3 g urea is dissolved in 45 g of water. What will be the relative lowering of vapour pressure?

(iii) A solution of 2.5 g of a non-volatile solid in 100 g benzene is boiled at 0.42 °C higher than the boiling point of pure benzene. Calculate the molecular mass of the substance. Molal elevation constant of benzene is 2.67 K kg mol^{-1}.

OR

(i) Define van't Hoff factor.

(ii) State Henry's law and mention two of its important applications.

(iii) Differentiate between molarity and molality of a solution. How can we change molality value of a solution into molarity value?

SOLUTIONS

1. For the solid *AB*, having NaCl structure,

$$\frac{r_{A^+}}{r_{B^-}} = 0.414 - 0.732$$

or Maximum possible value of

$$r_{B^-} = \frac{r_{A^+}}{0.414} = \frac{120 \text{ pm}}{0.414} = 290 \text{ pm}$$

2. Water is a volatile solvent. When a non-volatile solute such as glucose is added to it, then its vapour pressure is lowered.

3. Frenkel defect, because size of Zn^{2+} ions is quite small as compared to that of S^{2-} ions.

4. The binary solution which at some definite composition boil at constant temperature like a pure liquid and possess the same composition of components in liquid (solution) as well as in vapour phase are called azeotropic mixtures or azeotropes.

5. Crystal systems are

(i) tetragonal **(ii)** hexagonal.

6. Vapour pressure of pure benzene (p°) = 640 mmHg

Vapour pressure of solution (p_s) = 600 mmHg

Mass of solute (w_2) = 2.175 g

Mass of solvent, *i.e.*, benzene (w_1) = 39.0 g

Molecular mass of benzene, C_6H_6 (M_1) = 78 g

According to Raoult's law :

$$\frac{p^\circ - p_s}{p^\circ} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

On putting the values, we get

$$\frac{640 - 600}{640} = \frac{2.175 \times 78}{M_2 \times 39} \Rightarrow M_2 = 69.6 \text{ g mol}^{-1}$$

7. (i) Glass is an amorphous substance, whereas quartz is a crystalline substance.
(ii) Glass has only short range order, whereas quartz has a long range order.
(iii) Glass is isotropic, *i.e.,* its mechanical, electrical and optical properties do not depend upon the direction of measurement. Quartz on the other hand is anisotropic, *i.e.,* its properties depend on the direction of measurement.
(iv) In quartz, the SiO_4 tetrahedra are linked to each other through Si–O–Si bonds in three-dimensions. In glass, SiO_4 tetrahedra are arranged randomly.
When molten quartz is cooled very rapidly, if forms glass.

8. Mass of H_2SO_4 per litre (dm^3) = 9.8 g
Molar mass of H_2SO_4 = 98 g mol^{-1}
Therefore, number of moles of H_2SO_4 per litre of solution $= \frac{9.8}{98} = 0.1$

Hence, molarity of H_2SO_4 solution = 0.1 M
As there are two equivalents per mole of H_2SO_4, therefore, normality of H_2SO_4 solution = 0.1 × 2 = 0.2 N

9. Density, $(\rho) = \frac{Z \times M}{N_A \times a^3}$

$Z_{fcc} = 4$ and $Z_{bcc} = 2$

$\therefore \quad \frac{\rho_{fcc}}{\rho_{bcc}} = \frac{(Z)_{fcc} \times (a)^3_{bcc}}{(Z)_{bcc} \times (a)^3_{fcc}} = \frac{4}{2} \times \frac{(3.0)^3}{(3.5)^3} = 1.259$

10. 21.3% (*w*/*v*) means 100 mL of the HCl solution contains 21.3 g of HCl.

$$\text{Molarity} = \frac{21.3 \text{ g HCl}}{100 \text{ mL solution}} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$
$$= 5.8 \text{ M}$$

OR

250 mL of a 0.15 M solution will contain
250 mL × 0.15 mmol/mL = 37.5 mmol of benzoic acid.
∴ The mass of benzoic acid required
= 37.5 mmol × 122 mg/mmol
= 4575 mg = 4.575 g

11. A cubic close-packed structure is a *fcc* structure. For a face-centred cubic lattice,

face diagonal = $a\sqrt{2} = 4r$
(*a* is the edge length of the unit cell)

(i) For aluminium, $a = \frac{4}{\sqrt{2}} \times 125 \text{ pm}$
$= 353.6 \text{ pm} = 3.536 \times 10^{-8} \text{ cm}$

(ii) No. of unit cells in 1 cm^3 of aluminium
$= \frac{\text{Volume of element}}{\text{Volume of unit cell}} = \frac{1.00 \text{ cm}^3}{(3.536 \times 10^{-8} \text{ cm})^3}$
$= 2.26 \times 10^{22}$ unit cells

12. If acetic acid molecules exist in normal molecular state, then normal (calculated) ΔT_f would be

$\Delta T_f = K_f \cdot m \quad ; \quad \Delta T_f = 5.12 \times 0.1 = 0.512$ K

But the experimentally observed value of $\Delta T_f = 0.256$ K
Thus, the observed value of depression in freezing point (a colligative property) is half of the normal, theoretical value. It means that the number of 'particles' actually present in the solution, is half of the theoretical value. Therefore, acetic acid exists as doubly associated molecules or as dimers $(CH_3COOH)_2$ in benzene.

13. (i) In hexagonal close packing, the sphere of third layer lie directly above those in first layer. This leads to a pattern of the type *AB AB AB*.... .
In the cubic close packing, the spheres of fourth layer will corresponds to those in first layer. This leads to a pattern of the type *ABC ABC ABC*.... .
(ii) A regular arrangement of points (each representing an atom, ion or a molecule), in three dimensions is called a crystal lattice.
A unit cell is the smallest, but complete unit in a crystal lattice which when repeated in three dimensions generates the crystal lattice.
(iii) A tetrahedral void is formed when one sphere (or particle) is placed in the depression formed by three particles placed in a plane.
An octahedral void is formed when three close-packed spheres forming an equilateral triangle are placed over another similar set of three spheres, in opposite direction. Thus, the empty space at the centre of six spheres placed octahedrally is the octahedral void.

14. (i) The hydrostatic pressure exerted on the solution which just prevents the passage of solvent into the solution through a semi-permeable membrane, is called the osmotic pressure of the solution.
(ii) Osmotic pressure, $\pi = (500/76)$ atm
Temperature, $T = (27 + 273) = 300$ K
Mass of solute, $w = 4$ g
Volume of solution, $V = 100 \text{ cm}^3 = 0.1$ L
$R = 0.0821$ L atm K mol^{-1}

We know, $\pi V = \frac{w}{M} RT$

$\therefore \quad M = \frac{w}{\pi V} \times RT = \frac{4 \times 0.0821 \times 300}{(500/76) \times 0.1}$ g/mol
$= 149.7$ g/mol

15. (i) In each unit cell, the number of Ca^{2+} ions = 1,

Ti^{4+} ions = $\frac{1}{8} \times 8 = 1$, O^{2-} ions = $\frac{1}{4} \times 12 = 3$

Thus, the formula unit of perovskite is $CaTiO_3$.

(ii) Each corner is shared among 8 unit cells, so the contribution of a corner atom to any particular unit cell is 1/8. Hence, the number of Q atoms in a unit cell = $\frac{1}{8} \times 8 = 1$

The number of P atoms in a unit cell = 1

So, P and Q should be present in the same proportion in the compound and the formula of the compound is PQ. All the Q atoms are at the same distance from the P atom at the body-centre, so the coordination number of P is 8. Since P and Q are in proportion 1 : 1 in the compound, their coordination numbers must be equal. So, the coordination number of $Q = 8$.

16. (i) 86% H_2SO_4 means 100 g of the solution contains 86 g of sulphuric acid.

$$\text{Volume of the 100 g of acid} = \frac{\text{Mass}}{\text{Density}} = \frac{100\text{ g}}{1.787\text{ g/mL}} = 55.9\text{ mL}$$

$$\text{Moles of solute} = \frac{86}{98}$$

$$\text{Molality} = \text{moles of solute} \times \frac{1000}{\text{Vol. of solution (mL)}}$$

$$= \frac{86}{98} \times \frac{1000}{55.9} = 15.7\text{ M}$$

(ii) $M_1V_1 = M_2V_2$

$15.7 \times V_1 = 0.2 \times 1000$

$\therefore\ V_1 = \frac{0.2 \times 1000}{15.7} = 12.74$ mL

(iii) Mass of the solution = 100 g

Mass of the solute = 86 g

Mass of the solvent = 100 – 86 = 14 g

$$\text{Molality} = \text{moles of solute} \times \frac{1000}{\text{Wt. of solvent (g)}}$$

$$= \frac{86}{98} \times \frac{1000}{14} = 62.68\text{ m}$$

17. (i) The cubic close packing has a face-centred cubic unit cell. I^- ions occupy the corners and the face centres. These ions touch each other along the face diagonal of the cube. Hence,

$4r_{I^-} = \sqrt{2}a$

$$r_{I^-} = \frac{a}{2\sqrt{2}} = \frac{624}{2(1.414)} = 220.65\text{ pm}$$

Now, along the edge, there is I^- Li^+ I^- arrangement, where I^- ions are at the corners and Li^+ ions at the centre of the edge (octahedral void). Since in closest packing, they touch each other, thus

$2r_{I^-} + 2r_{Li^+} = a$

$$r_{Li^+} = \frac{a}{2} - 2r_{I^-} = \frac{624}{2} - 220.65 = 91.35\text{ pm}$$

(ii) For body-centred cubic crystals,

$$r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 351\text{ pm} = 151.98\text{ pm}$$

18. Vapour pressure of heptane = 105.2 kPa

Vapour pressure of octane = 46.8 kPa

Mass of heptane = 25.0 g

Molar mass of heptane = 100 g/mol

Mass of octane = 35.0 g

Molar mass of octane = 114 g/mol

So, moles of heptane, $n_h = \frac{25.0\text{ g}}{100\text{ g/mol}} = 0.25$ mol

moles of octane, $n_o = \frac{35.0\text{ g}}{114\text{ g/mol}} = 0.31$ mol

Mole fraction of heptane,

$$x_h = \frac{0.25\text{ mol}}{0.25\text{ mol} + 0.31\text{ mol}} = 0.446$$

Mole fraction of octane,

$$x_o = \frac{0.31\text{ mol}}{0.25\text{ mol} + 0.31\text{ mol}} = 0.554$$

Now, Vapour pressure of the mixture,

$P = x_h \times p_h + x_o \times p_o$

$= 0.446 \times 105.2\text{ kPa} + 0.554 \times 46.8\text{ kPa}$

$P = 46.9\text{ kPa} + 25.9\text{ kPa} = 72.8\text{ kPa} = 0.728$ bar

19. (i) (a) Ferromagnetism : Substances which are very strongly attracted by the magnetic field are called ferromagnetic and this property is called ferromagnetism.

Examples : Iron, cobalt, nickel, gadolinium and CrO_2.

These substances can be permanently magnetised *i.e.,* they retain magnetic property even in absence of applied magnetic field.

(b) Paramagnetism : Materials which are weakly attracted by magnetic fields are called paramagnetic materials and this property is called paramagnetism.

Paramagnetic substances contain unpaired electrons. *e.g.,* TiO, CuO, O_2 and VO etc.

(ii) Ferrimagnetic substances have a net dipole moment due to unequal parallel and antiparallel alignment

of magnetic moments whereas antiferromagnetic substances have net magnetic moment zero due to compensatory alignment of magnetic moments. Therefore, ferrimagnetic substances show better magnetism than antiferromagnetic substances.

20. Since, the liquid mixture is equimolar in *A* and *B*, the mole fractions,

$$x_A = x_B = \frac{1}{2}$$

(i) $p_T = x_A p_A^o + x_B p_B^o$

$$= \frac{1}{2} \times 450 \text{ mm Hg} + \frac{1}{2} \times 375 \text{ mm Hg}$$

$$= 412.5 \text{ mmHg}$$

(ii) Mole fraction of *A* in vapour phase,

$$Y_A = \frac{p_A}{p_T} = \frac{x_A p_A^o}{x_A p_A^o + x_B p_B^o}$$

$$= \frac{(1/2) \times 450}{(1/2) \times 450 + (1/2) \times 375} = \frac{225}{412.5} = 0.54$$

(iii) The vapour will be equimolar if

$$x_A = \frac{p_B^o}{p_A^o + p_B^o} = \frac{375 \text{ mm}}{450 \text{ mm} + 375 \text{ mm}} = \frac{375}{825} = 0.454$$

Suppose *n* mol of *B* is required to be mixed with 1 mol of *A*. Then,

$$X_A = \frac{1}{1+n} = 0.454$$

$$\Rightarrow \quad n = \frac{1 - 0.454}{0.454} = \frac{0.546}{0.454} = 1.20 \text{ moles}$$

Hence, 1.20 moles of *B* should be mixed with 1 mol of *A* for the vapour to be equimolar in *A* and *B*.

21. (i) Some of the glass objects from ancient monuments look milky instead of being transparent because it undergoes heating during the day and cooling at night *i.e.*, annealing over a number of years.
As a result, it acquires some crystalline character and become a bit opaque.

(ii) Differences between crystalline and amorphous solids are as follows :

	Crystalline solid	Amorphous solid
1.	It has definite characteristic geometrical shape.	It has irregular shape.
2.	It has sharp melting point. *e.g.*, sodium chloride (NaCl).	It melts over a range of temperature. *e.g.*, plastic.

OR

$$\rho = \frac{Z}{a^3}\left(\frac{M}{N_A}\right)$$

where, ρ = density = 2.165 g cm^{-3}
M = molar mass = 58.5
N_A = Avogadro's number = 6.023×10^{23}
Z = number of formula unit per unit cell
= 4 (for *fcc*)
a = Edge length

$$a^3 = \frac{Z}{\rho}\left(\frac{M}{N_A}\right) = \frac{4}{2.165}\left[\frac{58.5}{6.023 \times 10^{23}}\right]$$

$$= 1.794 \times 10^{-22}$$

$$a = 5.64 \times 10^{-8} \text{ cm}$$

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}} = \frac{58.5}{2.165} = 27$$

Edge length (a) = $(27)^{1/3}$ = 3 cm for 1 mol of NaCl

22. (i) Mass of urea = 15 g
Molar mass of urea = 60 g mol^{-1}
Molar mass of glucose = 180 g mol^{-1}
Mass of glucose = ?
For isotonic solution, osmotic pressure, $\pi_1 = \pi_2$

$n_1 = n_2$ (when volume is same)

or $\frac{W_1}{M_1} = \frac{W_2}{M_2} \Rightarrow \frac{15}{60} = \frac{W_2}{180} \Rightarrow W_2 = \frac{15 \times 180}{60} = 45$ g

(ii) According to Henry's law, $p = K_H x$

or $x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{0.987}{76.48 \times 10^3} = 1.29 \times 10^{-5}$

where n is the number of moles of N_2 in solution and moles of water contains (1000/18) = 55.5, then

$$x_{N_2} = \frac{n}{n + 55.5} \approx \frac{n}{55.5} = 1.29 \times 10^{-5}$$

$\therefore \quad n = 55.5 \times 1.29 \times 10^{-5} = 7.16 \times 10^{-4}$ mol

or $\quad = 7.16 \times 10^{-1}$ mmol = 0.716 mmol

23. (i) The defects which lead to a variable composition and the violation of the law of definite proportions. Compounds with such defects are called non-stoichiometric compounds or berthollides. One example of a berthollide is the mineral wustite, which is nominally FeO, and has a composition in the range of $Fe_{0.93}O$ to $Fe_{0.96}O$.

(ii) Let 1 mol of the oxide contain x mol of Fe(III). Then, the total positive charge in 1 mol of the crystal

$$= N_A x \times 3 + N_A(0.96 - x) \times 2$$

The total negative charge in 1 mol of the crystal = $N_A \times 2$
Since, the total positive and negative charges must be equal, *i.e.*, $N_A.x \times 3 + N_A(0.96 - x) \times 2 = N_A \times 2$
$\Rightarrow \quad 0.96 \times 2 + x = 2$
$\Rightarrow \quad x = 2 - 0.96 \times 2 = 0.08$
Thus, out of a total of 0.96 mol of iron atoms, 0.08 mol are Fe(III).
$\therefore$ the fraction of Fe(III) atoms

$$= \frac{\text{Fe (III)}}{\text{Total Fe}} = \frac{0.08 \text{ mol}}{0.96 \text{ mol}} = 0.0833$$

24. (i) In a face-centred cubic lattice, anions touch each other along the face diagonal of the cube.

$4r_{Cl^-} = \sqrt{2}a$

$$r_{Cl^-} = \frac{\sqrt{2}}{4}a = \frac{\sqrt{2}}{4} \times 5.14 = 1.82 \text{ Å}$$

(ii) Number of atoms $= \dfrac{\text{Mass}}{\text{Atomic mass}} \times N_A$

$$= \frac{39}{39} \times N_A = N_A$$

In *bcc* unit cell, $Z = 2$

$\therefore$ Number of unit cells $= \dfrac{N_A}{2} = 0.5\, N_A$

(iii) According to Henry's law, $C = K_H \,.\, p$
Where given $K_H = 3.1 \times 10^{-2}$ mol L^{-1} atm^{-1}
$p = 3.8 \times 10^{-4}$ atm
Hence, $C = 3.1 \times 10^{-2} \times 3.8 \times 10^{-4} = 1.18 \times 10^{-5}$ mol L^{-1}.

25. (i) (a) Partially soluble (b) Insoluble
(c) Soluble (highly) (d) Soluble
(e) Insoluble (f) Partially soluble
(ii) Conc. of aq. solution of nalorphene
$= 1.5 \times 10^{-3}$ mol kg^{-1}
Molar mass of nalorphene $= (19 \times 12 + 21 \times 1 + 14 + 3 \times 16)$
$= 311$ g/mol
Mass of nalorphene $= 1.5 \times 10^{-3}$ mol $kg^{-1} \times 311$ g mol^{-1}
$= 0.466$ g/kg of water
$= 466$ mg/kg of water
Total mass of the solution $= 1000$ g $+ 0.466$ g
$= 1000.47$ g
Mass of solution for a dose $= \dfrac{1000.47 \text{ g}}{466 \text{ mg}} \times 1.5 \text{ mg} = 3.2$ g

OR

(i) This is because the acid strength of the given acids follows the order.
Trifluoroacetic acid > Trichloroacetic acid > Acetic acid
Fluorine is more electronegative than chlorine. So, trifluoroacetic acid is stronger than trichloroacetic acid. As a result, the extent of ionisation, the concentration of ions and hence the depression in freezing point also follows the order same as given above.
(ii) Eq. wt. of HCl = mol. wt. of HCl = 36.5
Wt. of HCl in 1 litre of N/2 HCl $= 36.5 \times 1/2$ g $= 18.25$ g
Weight of HCl lost on heating $= 2.675$ g
$\therefore$ Weight of HCl left in solution $= 18.25 - 2.675$ g
$= 15.575$ g

36.5 g of HCl = 1 g equivalent

$$15.575 \text{ g of HCl} = \frac{1}{36.5} \times 15.575 \text{ g eq.}$$

Volume of the resultant solution = 750 mL

$$= \frac{750}{1000} \text{ L} = 3/4 \text{ L}$$

$\therefore$ Normality of solution $= \dfrac{\text{g. eq. of solute}}{\text{Vol. of solution in L}}$

$$= \frac{15.575 / 36.5}{3/4} = 0.57$$

Equivalents of HCl in 1000 mL of the original solution $= 1/2$
$\therefore$ Milliequivalent of HCl in 1000 mL $= 1/2 \times 1000$
$= 500$
$\therefore$ Milliequivalent of HCl in 100 mL $= \dfrac{500 \times 100}{1000} = 50$

26. (i) (a) $a\sqrt{3} = 4r$ where, a = edge length

$$r = \frac{a\sqrt{3}}{4} = \frac{2.93 \times \sqrt{3}}{4} = 1.268 \text{ Å}$$

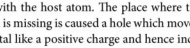
(b) Distance between the centres of neighbouring spheres $= 2r = 2 \times 1.268 = 2.536$ Å
(c) No. of atoms per unit cell (*bcc*) $= 8 \times \dfrac{1}{8} + 1 = 2$
(ii) One cation of Sr^{2+} would create one cation vacancy in NaCl. Therefore, the number of cation vacancies created in the lattice of NaCl is equal to the number of divalent Sr^{2+} ions added.
$\therefore$ Concentration of cation vacancy on being doped with 10^{-3} mol% $SrCl_2 = 10^{-3}$ mol% $= \dfrac{10^{-3}}{100} = 10^{-5}$ mol
Number of Sr^{2+} ions in 10^{-5} mol $= 10^{-5} \times 6.023 \times 10^{23}$
$= 6.023 \times 10^{18}$ Sr^{2+} ions
Number of cation vacanceis $= 6.023 \times 10^{18}$

OR

(i) The solids which have conductivities between 10^{-6} to 10^{4} ohm^{-1} m^{-1} are called semiconductors. *e.g.*, germanium and silicon. The two main types of semiconductors are as follows :

(a) ***n*-type semiconductor :** When a silicon crystal is doped with atoms of group-15 elements, such as P, As, Sb or Bi then only four of the five valence electrons of each impurity atom participate in forming covalent bonds and fifth electron is almost free to conduct electricity. Group-14 elements doped with a group-15 elements are called *n*-type semiconductors.

(b) ***p*-type semiconductor :** When a silicon crystal is doped with atoms of group-13 elements, such as B, Al, Ga or In. Each impurity atoms form only three covalent bonds with the host atom. The place where the fourth electron is missing is caused a hole which move through the crystal like a positive charge and hence increases its conductivity. Group-14 elements doped with group-13 elements are called *p*-type semiconductors.



n-type semiconductor *p*-type semiconductor

(ii) (a) Frenkel defect does not alters the density of solid.

$$d = \frac{M \times Z}{a^3 \times N} = \frac{40 \times 4}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}}$$

$$= 1.5455 \text{ g/cm}^3$$

(b) Schottky defect lowers the density of solid.

$$Z = 4 - \frac{4 \times 0.1}{100} = 3.996$$

$$d = \frac{40 \times 3.996}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}} = 1.5440 \text{ g/cm}^3$$

27. (i) Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as colligative properties. The colligative properties are :

(a) Lowering in the vapour pressure,

(b) Elevation in the boiling point.

(ii) Mass of urea (NH_2CONH_2) = 60 g mol^{-1}

Moles of urea (n_B) = $\frac{3}{60}$ = 0.05;

Moles of water (n_A) = $\frac{45}{18}$ = 2.5

$$\frac{\Delta p}{p^0} = x_B = \frac{n_B}{n_A + n_B} = \frac{0.05}{2.5 + 0.05} = 0.0196 = 0.02$$

(iii) Molecular mass (M)= $\frac{1000 K_b \times w}{W \times \Delta T_b}$

Given, $K_b = 2.67$, $w = 2.5$ g, $W = 100$ g, $\Delta T_b = 0.42$

$$M = \frac{1000 \times 2.67 \times 2.5}{100 \times 0.42} = 158.9 \text{ g}$$

OR

(i) van't Hoff factor : It is the ratio of the experimental value of colligative property to the calculated value of the colligative property and is used to find out the extent of dissociation or association. Mathematically, it is represented as

$$i = \frac{\text{Experimental (or observed value) of colligative property}}{\text{Calculated (or normal value) of colligative property}}$$

(ii) Henry's law states that 'the partial pressure of the gas in vapour phase (p) is directly proportional to the mole fraction of the gas (x) in the solution.'

$p = K_H \cdot x$; where, K_H = Henry's law constant. Different gases have different K_H values at the same temperature.

Applications of Henry's law :

(i) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

(ii) To minimise the painful effects of decompression sickness in deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.

(iii)

Molarity	Molality
Number of moles of solute dissolved in one litre solution is called molarity.	Number of moles of solute dissolved in one kg solvent is called molality.
Molarity depends on temperature as volume depends on temperature. Molarity decreases with rise in temperature.	Molality is independent of temperature as mass does not change with temperature.

If M_B is the molar mass of solute, d is the density of solution then molarity (M) value of a solution can be converted into its molality (m) by using the following formula,

$$m = \frac{1000 \times M}{(1000 \times d) - (M \times M_B)}$$

YOU ASK WE ANSWER

Do you have a question that you just can't get answered?

Use the vast expertise of our MTG team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough. The best questions and their solutions will be printed in this column each month.

1. Why peroxide effect is effective only in the case of HBr but not in case of HCl and HI?

(S.Krithika, Kerala)

Ans. H−Cl bond (103 Kcal/mol) is stronger than H−Br (87 Kcal/mol), thus H−Cl is not decompose by peroxide-free radical. In case of H−I, iodine free radical is formed as H−I bond is weaker but iodine free radicals readily combine with each other to form I_2 molecules rather than to attack the double bond.

In free radical mechanism for H−Br, both the chain propagation steps are exothermic, hence peroxide effect is observed, while in HCl, the second step is endothermic and in case of HI, the first step is endothermic therefore, peroxide effect is not observed in HCl and HI.

2. Primary amines form alcohols (1°, 2° and 3°) with nitrous acid (NaNa2 + HCl) but methyl amine cannot be used to for methyl alcohol. Why?

(Mohd. Jawed, Hyderabad)

Ans. Primary amine form alcohols with nitrous acid with the elimination of N_2 gas (brisk effervescence) and a clear solution if obtained.

$$RNH_2 \xrightarrow{HONO} ROH + N_2\uparrow + H_2O$$

(R = ethyl, propyl, etc.)

Methyl amine (also a 1° amine) is an exception to this reaction. With excess of nitrous acid, methylamine does not yield methyl alcohol only but can also form methyl nitrile or dimethyl ether *i.e.*,

$$CH_3NH_2 + 2HONO \longrightarrow \underset{\text{Methyl nitrile}}{CH_3ON} = O + N_2 + 2H_2O$$

$$2CH_3NH_2 + 2HONO \longrightarrow \underset{\text{Dimethyl ether}}{CH_3OCH_3} + 2N_2 + 3H_2O$$

3. Oxysalts of transition elements are found to be coloured even they do not have unpaired electrons in their valance shells? *(Jerin, Karnataka)*

Ans. The central atom of the oxysalts of transition elements like $K_2Cr_2O_7$, $KMnO_4$ do not have unpaired electrons in but they are deep in colour. The colour of these compounds is due to charge transfer spectrum. In these ions, transition of electrons occurs from orbital of one atom to the orbital of another atom by absorbing radiation to produce dark colour. As this transition occurs in UV region thus UV region is known as charge transfer region.

Lets observe some examples of silver

	AgCl	AgBr	AgI	Ag_2S
Colour	White	Pale yellow	Yellow	Black
% Ionic character	80%	24%	15%	4%

$Ag^+ - [kr]4d^{10}5s^0$

There is no unpaired electron with Ag^+. Thus, colour of these compound can be explain on the basis of % ionic character.

If the ionic character of these compounds is less than 20% then the compound will be coloured.

4. Why aromatic halides cannot be used? Then how can be prepare aromatic ethers?

(Mahesh singh, Harayana)

Ans. Aryl halides and sodium alkoxide cannot be used for preparing phenolic ethers because aryl halides are much less reactive towards nucleophilic substitution reactions than alkyl halides. The C−X bond acquires a double bond character (due to resonance).

Bromobenzene

$$+ Na^+ O^-CH_3 \longrightarrow \text{No reaction}$$

sod. methoxide

In that case, Dimethyl sulphate or diethyl sulphate can be used in place of halide in williamson synthesis (for aliphatic as well as aromatic ethers).

$$C_2H_5O^-Na^+ \longrightarrow C_2H_5O^- + Na^+$$

$$C_2H_5O^- + \underset{\text{Dimethyl sulphate}}{CH_3-O-SO_3CH_3} \longrightarrow \underset{\text{Ethyl methyl ether}}{C_2H_5-O-CH_3} + CH_3OSO_3^-$$

or $$C_2H_5ONa + \underset{\text{Diethyl sulphate}}{(C_2H_5)_2SO_4} \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + C_2H_5SO_4^-Na^+$$

$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Diethyl sulphate}}{(C_2H_5)_2SO_4} \xrightarrow[\Delta]{2NaOH_{(aq)}} \underset{\text{(Ethyl phenyl ether)}}{C_6H_5OC_2H_5} + Na_2SO_4 + 2H_2O$$

Phenetol

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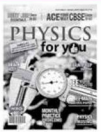

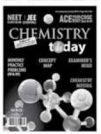

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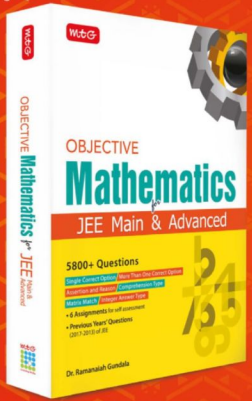

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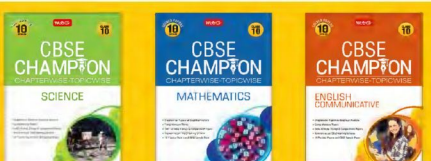

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